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TECHNICAL REPORT
DEPARTMENT OF PHYSICS
UNIVERSITY OF CALIFORNIA

LOS ANGELES

CONTRACT RESEARCH

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SOUND ABSORPTION IN
MAGNESIUM SULPHATE SOLUTIONS

by
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Technical Report No. VI

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Submitted by
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I. Introduction

Statement of the Problem

R. W. Leonard [5] has shown that the difference in the sound absorption in sea water and in fresh water at frequencies below one megacycle is due largely to the presence in the sea of magnesium sulphate. L. Liebermann [7] has proposed that either a unimolecular or a dissociation type process involving magnesium sulphate molecules or its ions might be the cause of the excess sound absorption. The work of O. B. Wilson [4] seemed to show that the process was unimolecular but as pointed out by R. Barthel [8], some errors had been made which when corrected showed that Wilson's data fitted equally well either the unimolecular or the dissociation process.

In an effort to determine the mechanism responsible for the excess sound absorption in magnesium sulphate solutions at frequencies below one megacycle a new parameter has been introduced. On the suggestion of Dr. Leonard the effect on the acoustic phenomenon of varying the dielectric constant of the solvent has been studied. This should shift the dissociation equilibrium and should have a marked effect on the sound absorption.

The theoretical treatments so far published have been inadequate since they have not taken into account the strong dependence of the activities of the ions on their concentration. This was pointed out by Dr. Leonard Hall in a private conversation. On his

suggestion equations have been derived which take into account this effect. It appears from the present work that the effect of the variation in activities due to the variation in local concentration with the passage of a sound wave is certainly not negligible.

In the following pages will be presented quantitative reasons for believing that the excess sound absorption in magnesium sulphate solutions at frequencies between five and five hundred kilocycles and for concentrations between one thousandth and twenty thousandths molar is due to an irreversible periodic perturbation of the simple dissociation process.

Sound Absorption Due To Relaxation

Suppose that a sinusoidal plane wave sound field is moving in the positive x direction in a dissipative medium. The sound pressure p in complex notation at any point along the x axis in terms of the sound pressure p_0 at the origin is

$$p = p_0 \exp. i\omega(t-x/v) = p_0 \exp. [-ax + i\omega(t-x/v_0)] \quad (1)$$

where ω is the angular frequency, t is the time, v_0 is the sound velocity, a is the pressure attenuation coefficient and v is the complex velocity equal to $v_0^{-1} - i a \omega^{-1}$.

The sound intensity is proportional to the square of the pressure amplitude so that the intensity of the sound I at any point along the x axis in terms of the sound intensity I_0 at the origin is

$$I = I_0 \exp. -2ax \quad (2)$$

where $2a$ is the intensity attenuation coefficient in nepers per unit of length.

Consider a uniform continuous isotropic medium, the particles of which may exist in one or the other of two possible states A and B. These states might be characterized by different energy levels or geometrical configurations involving different volumes or be characterized by a combination of both properties.

Suppose that the two states are in dynamic equilibrium with each other so that particles in state A are continually going over to state B and vice versa such that the relative populations in the two states form a constant ratio K' .

In general K' will be a function of the temperature T , of the pressure P , of the composition expressed in moles per liter c , and of the forces of interaction of the particles. For electrolytes the coulombic forces of the ions in solution on each other are so strong that other intermolecular forces may be neglected to the first approximation in comparison with them. The behavior of electrolytic solutions may thus be described with fair accuracy in terms of the ionic charges z_1 and the dielectric constant D of the medium. For electrolytes one may write symbolically

$$A \rightleftharpoons B \quad (3)$$

$$B/A = K'(T, P, c, z_1, D) \quad (4)$$

where the explicit dependence of the equilibrium parameter K' on the variables depends upon the mechanism involved.

Consider an acoustic wave traveling through the medium. The passage of the sound wave past a reference point in the medium will be accompanied by a time variation in the pressure and in general by an accompanying time variation in the temperature. The equilibrium will be perturbed irreversibly and will give rise to attenuation of the acoustic wave.

For a sound of low frequency the equilibrium will tend to follow the perturbing force reversibly. On the other hand, the process will tend not to follow the perturbing force at all at very high frequencies. At some intermediate frequency a maximum in the degradation of energy per cycle will be produced by the irreversibly perturbed mechanism.

The intensity attenuation coefficient in all ordinary liquids except mercury may be accounted for by the viscous losses. In electrolytic solutions such as described here the additional loss of sound energy due to the perturbed chemical equilibrium must be added to the viscous losses.

Analytically it is found that the contribution to the intensity attenuation coefficient tends to a constant value at infinite frequency and goes as the square of the frequency at low frequencies. The expression for the intensity attenuation coefficient may be written as

$$2\alpha = \frac{(2\mu' + \mu'')\omega^2}{2\rho v_0^3} + \frac{A'\omega^2}{\kappa^2 + \omega^2} \quad (5)$$

where the first term is due to viscosity and the second to chemical relaxation. The second term is called the excess absorption coef-

ficient.

μ' and μ'' are the shear and dilatational viscosity coefficients [9], ρ is the density, and A' and κ are physical constants characteristic of the perturbed chemical mechanism.

κ is the relaxation frequency measured in angular cycles per second. Physically it is the reciprocal of the time for the equilibrium parameter to come to $1/e$ of its final value when the system has been suddenly perturbed and then allowed to relax. e is the base of the napierian logarithms.

In writing equation (5) it has been explicitly assumed that the effect of the presence of the electrolyte is merely to add to the attenuation coefficient of the medium a term due to the perturbed mechanism. The assumption has also been made that there is only one such mechanism. Experiment has shown [1,2,15], however, that there are at least two for some of the electrolytes so far investigated. For such electrolytes a third term similar to the second term in equation (5) must be added. However, for frequencies well below the second relaxation frequency equation (5) would become

$$2\alpha = \frac{2\mu' + \mu''}{2\rho v_0^3} + \frac{A'\omega^2}{\kappa^2 + \omega^2} + \frac{A''\omega^2}{\kappa_2^2} \quad (6)$$

Thus a mechanism of high relaxation frequency will make a negligible contribution if A'' is not too large. Magnesium sulphate falls into this category.

At frequencies high compared to the relaxation frequency equation (5) becomes

$$2a = \frac{(2\mu' + \mu'')\omega^2}{2\rho v_0^3} + A \approx \frac{(2\mu' + \mu'')\omega^2}{2\rho v_0^3} \quad (7)$$

Measurements in the ocean show that at frequencies above one megacycle the attenuation coefficient is practically the same as for fresh water. This tends to show that μ' and μ'' are relatively unaffected by the presence of the salts in solution. However, measurements of the absorption of sound in aqueous sodium acetate solutions at frequencies between ten and forty megacycles have shown that the effect of the electrolyte may be to decrease the total intensity attenuation coefficient below that of pure water. This is explained by interpreting the viscosity of water as a relaxation phenomenon and assuming that the salt has decreased its relaxation time [10].

In magnesium sulphate solutions experiment seems to show that equation (5) describes the behavior of the intensity attenuation coefficient accurately to within the experimental error over the frequency range from five to one thousand kilocycles [2,4,15].

The excess absorption coefficient multiplied by a wave length has a maximum value when the frequency of the acoustic wave is equal to the relaxation frequency. From equation (5) this quantity is related to A' as follows:

$$\mu = \frac{1}{2} A' \lambda \quad (8)$$

where λ is an acoustic wave length.

In the special case of a simple dissociation process of the type $AB \rightleftharpoons A + B$, one may write in place of equations (3) and (4) the following equations using the mass action equilibrium law.

$$c(1-\alpha)k_1 = c^2 f_{\pm}^2 \alpha^2 k_2 \quad (9)$$

$$K = (c f_{\pm}^2 \alpha^2) / (1-\alpha) \quad (10)$$

f_{\pm}^2 is the mean squared activity coefficient, c is the molar concentration of dissociating electrolyte, α is the degree of dissociation, and K is the mass action equilibrium constant. k_1 and k_2 are the specific rate constants. The concentration of (AB) is given by $c(1-\alpha)$ and the concentration of either (A) or (B) is given by $c\alpha$. Activity coefficients have been introduced in order to replace activities with the more convenient concentration terms.

If k_1 is the specific rate of going from state A to state B and k_2 is the reverse specific rate then it may be expected that the relaxation frequency will be a function of k_1 and k_2 . One may also expect that if either one or both of the specific rate constants increases that the relaxation frequency will likewise increase. Since k_1 and k_2 both have the same units in time as κ (inverse seconds) it may be expected to involve these parameters in some linear combination, but since in general they may also have concentration units κ may be a function of the concentration c of the electrolyte as well.

The excess absorption cross section per wave length per mole μ/c may be expected to be a function of concentration as well as a function of the equilibrium parameter K' or of the mass action equilibrium constant K . If K' is zero then all particles are in state A and thus there can be no sound absorption. If K' is infinite then all particles are in state B and again there can be no sound absorption. Now since μ/c is a positive function of K' it

must pass through at least one maximum as K' goes from zero to infinity. For any simple system it seems reasonable that only one maximum will exist.

The dependence of κ and μ/c on the parameters c , K , k_1 , k_2 , and the temperature T is expressed symbolically in the following equations.

$$\mu/c = f(c, K, T) \quad (11)$$

$$\kappa = g(c, k_1, k_2, T) \quad (12)$$

The mechanism producing the excess sound absorption may be determined by determining the dependence of μ/c and κ on the parameters involved. In electrolytes k_2 and K may be varied by varying the total concentration of ions (ionic strength) in solution or the dielectric constant of the solvent [17].

Previous Work On Sound Absorption In Electrolytes

The most comprehensive work on excess sound absorption in electrolytes has been done by Tamm and Kurtze [1,2,15] and by Wilson [4]. The results of their work will be briefly reviewed. Tamm and Kurtze have investigated the acoustic absorption properties of a large number of electrolytes in water solutions with regard to the dependence of the absorption cross section and the relaxation frequency on the valence of the salt, the temperature, the concentration, the pH of the solution, and the effect of mixing of salts in solution. By using a spherical resonator in the range from 5 kc. to 50 kc., a reverberation method in the range from 50 to 1,000 kc., and Debye

type optical methods at higher frequencies they have managed to cover a frequency range from 5 kc. to 100 mc. Of principal interest here are the results obtained at frequencies below one megacycle and for the 2-2 valence type electrolytes.

All of the 2-2 valence type inorganic electrolytes investigated without exception showed large excess sound absorption. Tamm investigated the following sulphates: BeSO_4 , NiSO_4 , MgSO_4 , CoSO_4 , MnSO_4 , ZnSO_4 , and CuSO_4 . Wilson whose results confirm Tamm's investigated BeSO_4 , MgSO_4 , and ZnSO_4 . Tamm also investigated MgS_2O_3 and MgCrO_4 .

Tamm finds that for all of the 2-2 valence type inorganic electrolytes the excess sound absorption is approximately linearly dependent upon the concentration. In particular the absorption cross section of MgSO_4 , MnSO_4 , ZnSO_4 , and CuSO_4 is approximately constant over the range from .001 to .1 molar, but slightly diminishes at concentrations above approximately .1 molar.

Wilson has investigated the dependence of the excess sound absorption on concentration in somewhat more detail in the concentration range from .003 to .02 molar and finds a nonlinear relationship between the excess sound absorption and the concentration. In fact, it will later be shown that the absorption cross section μ/c calculated using Wilson's data tends to zero as the concentration goes to zero. Presumably Wilson's results because they are somewhat more detailed give a little better picture of the behavior of the absorption cross section at low concentrations than do Tamm's

for magnesium sulphate solutions.

The frequency dependence of the excess sound absorption for all of the electrolytes investigated showed that the effect may be interpreted in terms of one or more relaxation processes; in particular a relaxation frequency of 130 kc. at 20°C was determined for MgSO_4 which seemed to be independent of the concentration. A second relaxation process was also indicated at a frequency above 100 megacycles. NiSO_4 was found to have a relaxation frequency at about 15 kc., BeSO_4 a relaxation frequency below 10 kc. and CoSO_4 a relaxation frequency at about 400 kc. These relaxation frequencies were also found to be concentration independent. It was also determined that MgS_2O_3 and MgCrO_4 have about the same relaxation frequencies as MgSO_4 . Tamm concludes that the relaxation frequency seems to be determined by the cation (Mg^{++}) rather than by the anion (CrO_4^{--} , SO_4^{--} , $\text{S}_2\text{O}_3^{--}$) and is independent of concentration for a large number of electrolytes.

The effect on the excess sound absorption of MgSO_4 and MnSO_4 solutions of the addition of NaCl which shows no excess sound absorption of its own was also investigated. It was found that independent of the initial value of the absorption coefficient a_0 , the ratio of the incremental change Δa to the new value a was linearly related to the ratio of NaCl concentration to MgSO_4 concentration for both MgSO_4 and MnSO_4 . This was shown to be true for values of the ratio from 1 to 20. In particular Tamm reports the following empirical rule:

$$\Delta a / a = [(\text{NaCl})/(\text{MeSO}_4)] f \quad (13)$$

For MgSO_4 $f = 1/5$ and for MnSO_4 $f = 1/12.5$.

The temperature dependence of the relaxation frequency and the excess absorption cross section was investigated for NiSO_4 , CoSO_4 and for MgSO_4 . In each case it was found that the relaxation frequency increased with the temperature according to the law

$$\log(\kappa/T) = - (\Delta H/RT)\log(e) + \text{constant} \quad (14)$$

where ΔH is the enthalpy of activation and e is the napierian base. Wilson's work on the temperature dependence of the relaxation frequency gives good agreement with the work of Tamm for MgSO_4 .

The magnitude of the excess sound absorption cross section was observed by Tamm to increase very slightly and then to decrease as the temperature ranged from 11°C to 80°C for .05 molar MgSO_4 . Wilson investigated the temperature dependence of the excess absorption per wave length for a .01 molar solution of MgSO_4 and found a slight increase in the excess sound absorption between 4.4°C and 43.5°C in agreement with Tamm's results.

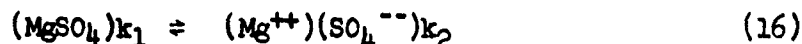
In an effort to explain his own results and those of Kurtze in the higher frequency range Tamm considers various possible models in the light of his evidence and comes to the conclusion that the excess sound absorption might be due to dissociation, ion association, or a complicated combination of molecular dissociation and hydrolysis. He rules out the possibility of thermal relaxation or of ion hydration. Tamm prefers the combination of molecular dissociation and hydrolysis hypothesis.

For magnesium sulphate Wilson ruled out the possibility of thermal relaxation since no appreciable decrease in the sound absorption was observed at about 4°C at which temperature the sound would be propagated approximately isothermally. This is in agreement with calculations due to Liebermann [7]. On this basis it will be assumed that the excess sound absorption is due to a pressure dependent process.

II. Theory of Sound Absorption in Magnesium Sulphate

As mentioned in the introduction, L. Liebermann [7] has proposed that the excess sound absorption in the sea may be due to the acoustical perturbation of either a unimolecular process involving the molecules or ions of magnesium sulphate or the dissociation process involving the same compound. The possible chemical mechanisms which he has suggested are

$$(A)k_1 \rightleftharpoons (B)k_2 \quad (15)$$



On the basis of (15) and (16) and the assumption of pressure dependence alone he has derived expressions for the excess sound absorption properties due to an irreversible perturbation of either the dissociation process or the unimolecular process where no account has been taken of activity coefficients. Barthel [8] has since presented similar equations in which he has considered activity coefficients for the dissociation process but not their variation with an acoustic wave.

For the unimolecular process of the type described by equation (15) the expressions for the maximum excess sound absorption per wave length and the relaxation frequency are according to Barthel

$$\mu = (\Delta V)^2 mk_1 k_2 / RT(k_1 + k_2)^2 \quad (17)$$

$$\kappa = \kappa_1 + \kappa_2 \quad (18)$$

m is the total concentration of the species producing the sound absorption. Since it is an experimental fact that both Mg^{++} and SO_4^{--} ions must be present we may take m as equal to either the concentration of pairs of ions $c\alpha$ or to the concentration of molecules $c(1-\alpha)$ where c is the concentration of magnesium sulphate and α is the degree of dissociation. (ΔV) is the change in volume per mole on going from state A to state B. β is the isothermal compressibility.

According to equation (18) the unimolecular process is characterized by a relaxation frequency which is independent of the concentration of electrolyte.

New equations for the maximum excess sound absorption per wave length and the relaxation frequency have been derived based upon the mechanism proposed in equation (16). The strong dependence of the activities of the ions on the concentration of the electrolyte and the periodic variation of the activities of the ions with the passage of an acoustic wave has been taken into account. These equations are based upon the assumption that an irreversible perturbation of a pressure dependent chemical equilibrium will cause a phase lag in the compressibility of the medium. No thermal relaxation is considered. The pseudo thermodynamic approach is used in the derivation which is given in the appendix.

In accounting for the variation of the activities with the passage of a sound wave a new function F is defined by means of equa-

tion (20) below. Through this equation the parameters dielectric constant D and ional concentration $\bar{\Gamma}$ are introduced. If c_i is the concentration of the i th ion species and z_i is the number of units of charge on it, then the ional concentration is given by the equation

$$\bar{\Gamma} = \sum_i c_i z_i^2 \quad [3] \quad (19)$$

and the function F is defined as follows:

$$F = -8 \frac{d \ln f_{\pm}^2}{d \bar{\Gamma}} \quad (20)$$

The function F is evaluated by means of the Debye Huckel equation for the mean activity coefficient [3].

$$\ln f_{\pm}^2 = - \frac{4.606 S \sqrt{\bar{\Gamma}}}{1 + A \sqrt{\bar{\Gamma}}} \quad (21)$$

The expressions for S and A are

$$S = 5.132 \times 10^6 (DT)^{-3/2} \quad (22)$$

$$A = 35.578 (DT)^{-1/2} \quad (23)$$

The mean ionic diameter \bar{a} enters into the calculation of A . The value used was taken as 3.08 angstroms (page 416 of reference 19). See the conclusion for a further discussion of the mean ionic diameter.

The function F always appears multiplied by c_{\pm} so that $F c_{\pm}$ shall be considered instead of F alone. $F c_{\pm}$ has been calculated and plotted as a function of c_{\pm} and is presented in graphical form in the appendix. The range of concentrations for which the expression for $F c_{\pm}$ is good is limited to the range for which equation (21) is applicable.

For the dissociation process the equations which have been derived (see the appendix) for the excess sound absorption per wave length per mole and the relaxation frequency are

$$\frac{\mu}{c} = \frac{\pi(1-\alpha) Wk_1}{\kappa \beta RT} \quad (24)$$

$$\kappa = k_1 \left[1 + \frac{(1-\alpha)}{\alpha} (2-Fc\alpha) \right] \quad (25)$$

β is the isothermal static compressibility of the medium and is assumed to be unchanged by the addition of the electrolyte. The determination of β is described in the appendix.

W is an empirical parameter which must be evaluated by experiment.

The following facts about the dependence of $Fc\alpha$ and α upon the dielectric constant D of the medium and the molar concentration c of the electrolyte in solution are pertinent to this experiment. The value of α decreases monotonically and for large values of the dielectric constant (water, $D = 78.5$ esu, $T = 25^\circ\text{C}$) very slowly from unity at zero concentration toward zero as the concentration increases. As the dielectric constant of the medium is lowered the rate of decrease of α with increasing concentration is greatly accelerated. This means with regard to equation (10) or (16) that the

value of the mass action equilibrium constant as well as the value of the mean squared activity coefficient is lowered by lowering the dielectric constant of the medium. Physically this means that the population of ions is diminished while the population of molecules is increased for a given total concentration of electrolyte as the dielectric constant is lowered.

The function F_{ca} plotted as a function of ca increases at first rapidly with concentration and then tends to level off increasing slowly at higher concentrations. The effect of lowering of the dielectric constant is to accelerate the rate of change of F_{ca} with c as well as to give it higher values. See the plot of F_{ca} in the appendix. It is shown in the appendix that F_{ca} is bounded.

In water solvents in the range of concentrations amenable to investigation with the present apparatus, the difference between equations (18) which predicts a constant relaxation frequency and (25) which predicts a slightly increasing one could not be definitely established because equation (25) increases only slightly and the dispersion in the measured values of κ was of the order of that increase. Dr. Wilson, like Tamm, concluded that the relaxation frequency was constant.

Similarly, Dr. Wilson's data for the excess absorption per wave length would fit either the dissociation or the unimolecular process as previously mentioned. From Wilson's data it may be shown that in magnesium sulphate solutions the ratio μ/c tends to zero as the concentration goes to zero. Thus this quantity is proportional to the number of magnesium sulphate molecules which

also tends to zero with the concentration.

If a unimolecular process were the source of the excess sound absorption then μ should be taken equal to $c(1-\alpha)$ according to the discussion above and equation (17) should take the form

$$\mu / c = \frac{\pi (\Delta V)^2 k_1 k_2}{(k_1 + k_2)^2} (1 - \alpha) \quad (26)$$

Since α is a monotonic decreasing function of concentration μ/c should be a monotonic increasing function for all c for the unimolecular case according to equation (26) while according to equation (24) for the dissociation case μ/c should increase at first to a maximum and then should decrease again. The work of Tamm taken together with that of Wilson shows the latter behavior for magnesium sulphate solutions.

If the range of values of α could be lowered then the differences between the two mechanisms would be quite marked in our limited range of concentrations. The relaxation frequency for the dissociation process would increase rapidly with concentration according to equation (25) while according to equation (18) it would remain constant for the unimolecular process. Further, the difference in the behavior of μ/c for the two cases would be quite different as mentioned above.

In order to distinguish between these two possible mechanisms on the one hand and to determine if the acoustic effect is due to either one of them on the other the range of values of α was lowered by lowering the dielectric constant of the medium. For this purpose

mixtures of dioxane and water as solvent instead of pure water were used. The results rule out the hypothesis of a unimolecular type mechanism and seem to confirm the assumption of a dissociation type mechanism instead.

Many different solvents mixed with water have apparently been used by chemists to determine the effect on the chemical kinetics of a reaction of the dielectric constant of the medium. For the purpose of the present study it was necessary to find a substance of low dielectric constant which was readily miscible in water and which did not produce an excessive increase in the sound absorption of the solvent.

It turns out that there are only about three substances suitable for this study [13]. These are dioxane, methanol, and ethylene glycol. Both ethylene glycol and dioxane have been tried but the experiments with the ethylene glycol have been unsuccessful. They are not reported here. The work with dioxane has been quite successful.

The work with ethylene glycol was complicated by the formation of a fine precipitate which could not be gotten rid of and the origin of which was not understood. Since the medium was quite viscous the precipitate remained in suspension in the medium. It is believed that these small particles added appreciably to the sound absorption of the medium so as to mask the expected relaxation effect. The results for ethylene glycol water solutions of magnesium sulphate could not be interpreted as a simple relaxation phenomenon.

III. Experimental Technique

Description of the Apparatus

The reverberation method is used. A frequency range of from about 20 kc. to 500 kc. and a range of decay rates from about 1 db/sec. to about 400 db/sec. is available with the apparatus used in this experiment. The reverberation method employed here has been described by Leonard [5] and by Tamm [15]. Mulders [16] and Moen [14] have also described similar techniques. Details of this particular apparatus have been given by Wilson [4] and by Leonard [5].

A closed spherical pyrex glass container filled with liquid and suspended on thin piano wires in a vacuum is used as the reverberation chamber. The sound source is a small ADP crystal glued on the outside of the bottle. The same crystal also acts as the sound receiver. By means of a system of relays a radio frequency generator feeds a signal of chosen frequency through an amplifier to the piezo electric crystal and thus stores acoustic energy in the resonator. When the sound level is sufficiently high the crystal is switched from the oscillator circuit to the receiving circuit. An RAK 7 radio receiver is used which beats the ultrasonic signal against a fixed frequency and thus produces an audible tone. The decay rate of the intensity of the audible tone is then used as a measure of the decay rate of the sound energy in the resonator.

The output signal is monitored visually by means of an oscillo-

scope with a long persistence screen fed by a logarithmic amplifier which gives a direct current voltage proportional to the logarithm of the sound intensity and audibly by means of a pair of earphones. The oscilloscope is synchronized to make one sweep when the decay signal is received.

For frequencies below about 300 kc. the decay rates are generally long enough to be recorded on a Brüel and Kjaer sound level recorder. For large decay rates and high frequencies the decay rate may be determined by calibrating the oscilloscope.

The resonators are round bottom pyrex boiling flasks whose necks have been reduced to about one inch high and one inch in outside diameter. Twelve liter boiling flasks were used throughout except for one series of measurements made on a .002 molar aqueous solution of magnesium sulphate in a 50 liter flask.

The crystals used were 45°Z cut ammonium dihydrogen phosphate crystals. For the frequency range from 20 to about 200 kc. it was found that a crystal of dimensions 2.0 x 1.2 x .6 cm. worked well while at frequencies above 200 kc. a pair of smaller crystals of dimensions approximately 1.0 x .8 x .6 cm. connected in parallel worked satisfactorily.

The temperature could be controlled to within plus or minus one half degree centigrade by means of a water jacket consisting of a large coil of copper tubing inside of the vacuum chamber. Thermal equilibrium between the contents of the resonator and the water jacket was assured by maintaining the temperature in the water jacket approximately constant for long periods of time. Further, the

temperature in the room always remained within a couple of degrees of 25°C.

The temperature of the resonator was measured by means of a calibrated thermister whose resistance was measured on a small Wheatstone bridge built for the purpose. The thermister was glued to the side of the resonator.

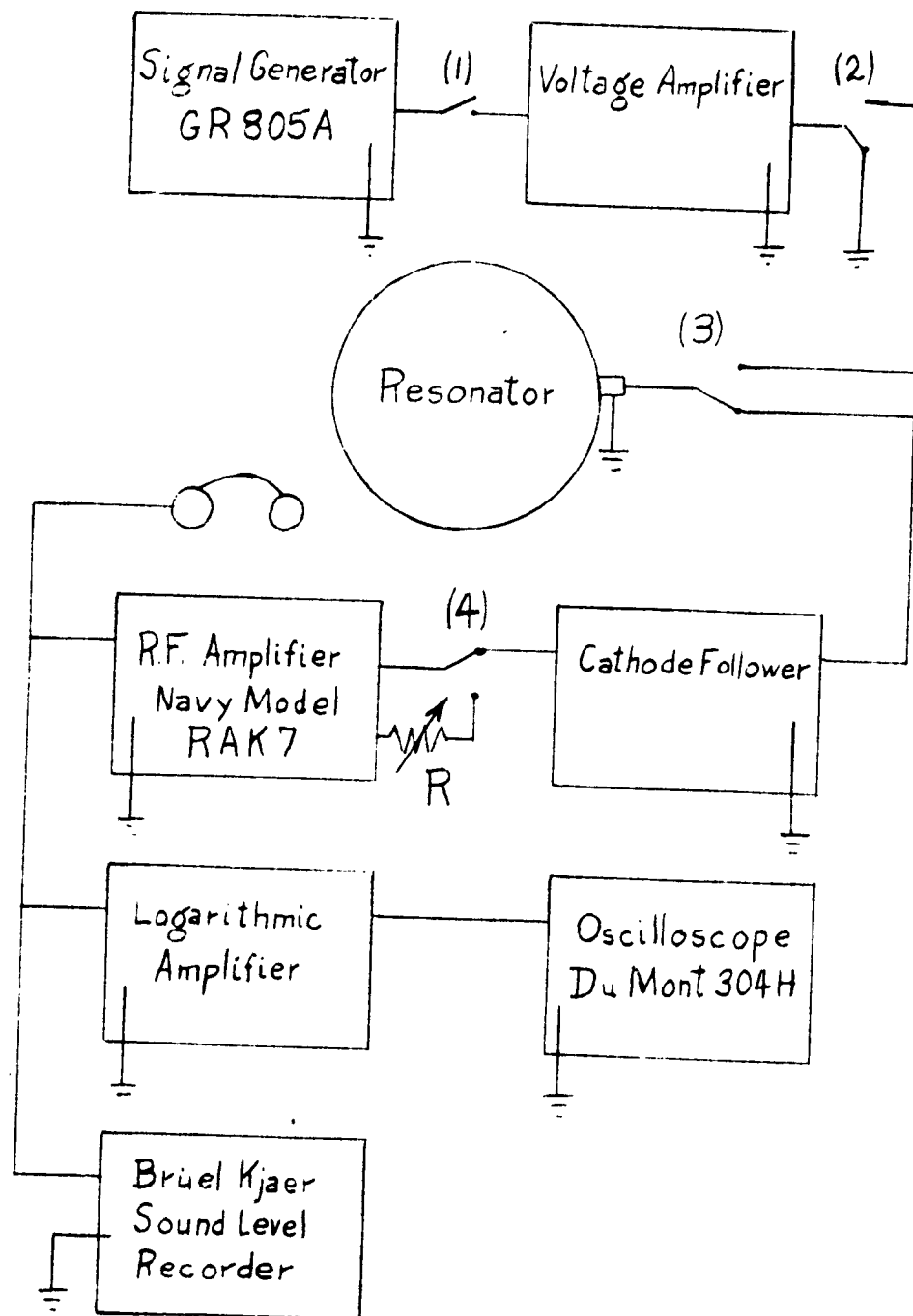
A schematic diagram of the electrical parts of the apparatus is given on the next page.

The system is normally in the receiving condition as shown in the diagram. When the system is keyed all of the relays (1), (2), (3) and (4) close and the system is in the send condition. A pick up signal whose intensity can be controlled by means of the variable resistance R is used to tune the receiver to the frequency of the signal generator. It is also used for auditory tuning of the signal generator to the resonant frequencies of the resonator.

Method of Taking Acoustic Data

In taking the data a selection process was used as follows. One starts at the top of the frequency scale and looks for a resonant mode. When one is found the trace on the oscilloscope will be a straight line. This decay rate is recorded and the oscilloscope is adjusted so that the trace makes a 45 degree line. One then goes down frequency looking for new modes which give straight line traces. If a mode is found with a trace steeper than 45 degrees it is rejected. If a mode is found with a trace less steep it is recorded and the

Schematic Diagram of Apparatus



oscilloscope is readjusted.

Both in theory and in practice a great number of modes of vibration of the resonator exist. Points corresponding to these decay rates plotted against frequency will form a kind of spread out domain. By the process described above one picks out the lowest of these modes and thus determines the least bound of this domain of points. It is believed that these points correspond to the radial modes of the resonator since for these modes the shear losses at the walls should be least and they should have the longest decay times. Empirically it is found that the least bound so obtained determines a reasonably smooth curve and that for pure solvent a straight line with a slope of two is determined for the frequency range from about 80 to 500 kc. Below about 80 kc. the wall losses become relatively large and the curve becomes less steep. Such curves are shown in the data.

Method of Determining μ and κ

First a series of reverberation measurements are made by means of the apparatus already described and a calibration of the resonator and liquid is obtained. Next magnesium sulphate is added as described in the appendix and the series of reverberation measurements is repeated. The increase in the sound absorption is attributed to the electrolyte. The total sound absorption is thus assumed to be the simple sum of the resonator and liquid losses plus the loss due to the perturbed chemical equilibrium. In particular equation (4) takes the form

$$2a = \frac{(2\mu' + \mu'')\omega^2}{2\rho v_0^3} - \frac{A'\omega^2}{\kappa^2 + \omega^2} + \text{wall losses} \quad (27)$$

The results of the calibration run are subtracted from the results with the salt to determine the excess sound absorption. In practice a kind of average curve is drawn through each of the two sets of points and the difference between these two curves is taken at regular intervals. Since the data is in db/sec. and the units of $2a$ are in nepers/cm. it is necessary to make a conversion of units.

If the excess sound absorption per wave length

$$\frac{A'\lambda\omega^2}{(\kappa^2 + \omega^2)} = \frac{.1151 [(\text{decay rate solution}) - (\text{decay rate solvent})]}{(\text{frequency})}$$

is plotted on a log log graph against the angular frequency the curve will take on a symmetrical form about a maximum value occurring at the relaxation frequency. The maximum excess absorption per wave length μ and the relaxation frequency κ are then easily determined from such a plot. Such curves are presented in the appendix with the data.

As defined κ is measured in angular cycles per second but the frequencies determined experimentally are measured in cycles per second; thus we must either multiply the relaxation frequency in cycles per second determined experimentally by 2π or divide κ by 2π . The latter course is the more convenient and will be followed here.

A summary of the results of a series of acoustic measurements is included in the appendix.

IV. Experimental Results

INFLUENCE OF THE DIELECTRIC CONSTANT

Results for Water, $D = 78.5$ esu, $T = 25^{\circ}\text{C}$

In order to test equations (24) and (25) the values of k_1 and W are calculated from the acoustical data and values of α calculated by using the activity coefficients of zinc sulphate (these should be quite similar to those of magnesium sulphate, reference 3) and the mass action equilibrium constant for an aqueous solution of magnesium sulphate at 25°C . The value of the mass action equilibrium constant was taken as .0063 from reference 6. Constancy of the calculated values of k_1 and W is expected on the basis of the dissociation hypothesis. The results of these calculations are tabulated below.

Calculated Values of $k_1/2\pi$ and W for Water
(25°C , $D = 78.5$ esu)

Concentration (moles/liter)	$k_1/2\pi$ (kc)	$W \times 10^3$ $\text{cm}^6/\text{mole}^2$
.002	114	6.04*
.003	107	5.53*
.0052	112	9.57
.008	110	9.07
.010	101	9.59
.014	107	8.81
.020	<u>116</u>	<u>8.82</u>
Average	109.6	Average 9.2

* These values are neglected in computing the average because of the large uncertainty in the values of excess sound absorption at these low concentrations.

Results for Water Dioxane Solvents

The values of the mass action equilibrium constants for solutions of dielectric constant equal to 67.0 and 56.5 esu were determined from the measured values of the relaxation frequency by means of equation (25). This was done in order to test equations (24) and (25) for the solutions of lower dielectric constant and to see if the acoustic data might be used to determine all of the parameters involved.

It was found that if the relaxation frequencies were plotted on a linear scale against the square root of the concentration that an approximately straight line could be drawn through the points and extrapolated to zero concentration. According to equation (25) the intercept on the frequency axis should give the value of k_1 . Equation (25) could then be solved for the degree of dissociation α for each particular value of concentration c . The activity coefficients could then be calculated and finally the mass action equilibrium constant could be calculated for each particular value of concentration. The extrapolated value of k_1 was adjusted until a value was found which would give the most nearly constant value of the mass action equilibrium constant for all of the concentrations on which measurements were made.

The solution of equation (25) was facilitated by a graphical technique. Equation (25) was solved for $F\alpha$.

$$F\alpha = \frac{2 - (1 + \kappa/k_1)\alpha}{1 - \alpha} \quad (29)$$

α on the right hand side of equation (29) was multiplied and divided by c which left the equation unchanged but made the right hand expression an explicit function of $c\alpha$ for fixed c . The right hand side of equation (29) was then plotted as a function of $c\alpha$ for fixed c and κ on a graph of $Fc\alpha$ versus $c\alpha$ similar to the one in the appendix. The intersection of the two curves gave the solution $c\alpha$ and $Fc\alpha$ directly. α was then computed from c and $c\alpha$.

Once α and $Fc\alpha$ were determined the values of W were calculated by means of equation (24) and the measured values of μ .

A plot of κ versus \sqrt{c} is included on the following page with the theoretical curves of best fit drawn in. A plot of μ/c versus \sqrt{c} is also included to show how these values follow the trend indicated by equation (24).

Results of Calculation

concentration (moles/liter)	K (moles/liter)	$W \times 10^3$ ($\text{cm}^6/\text{mole}^2$)
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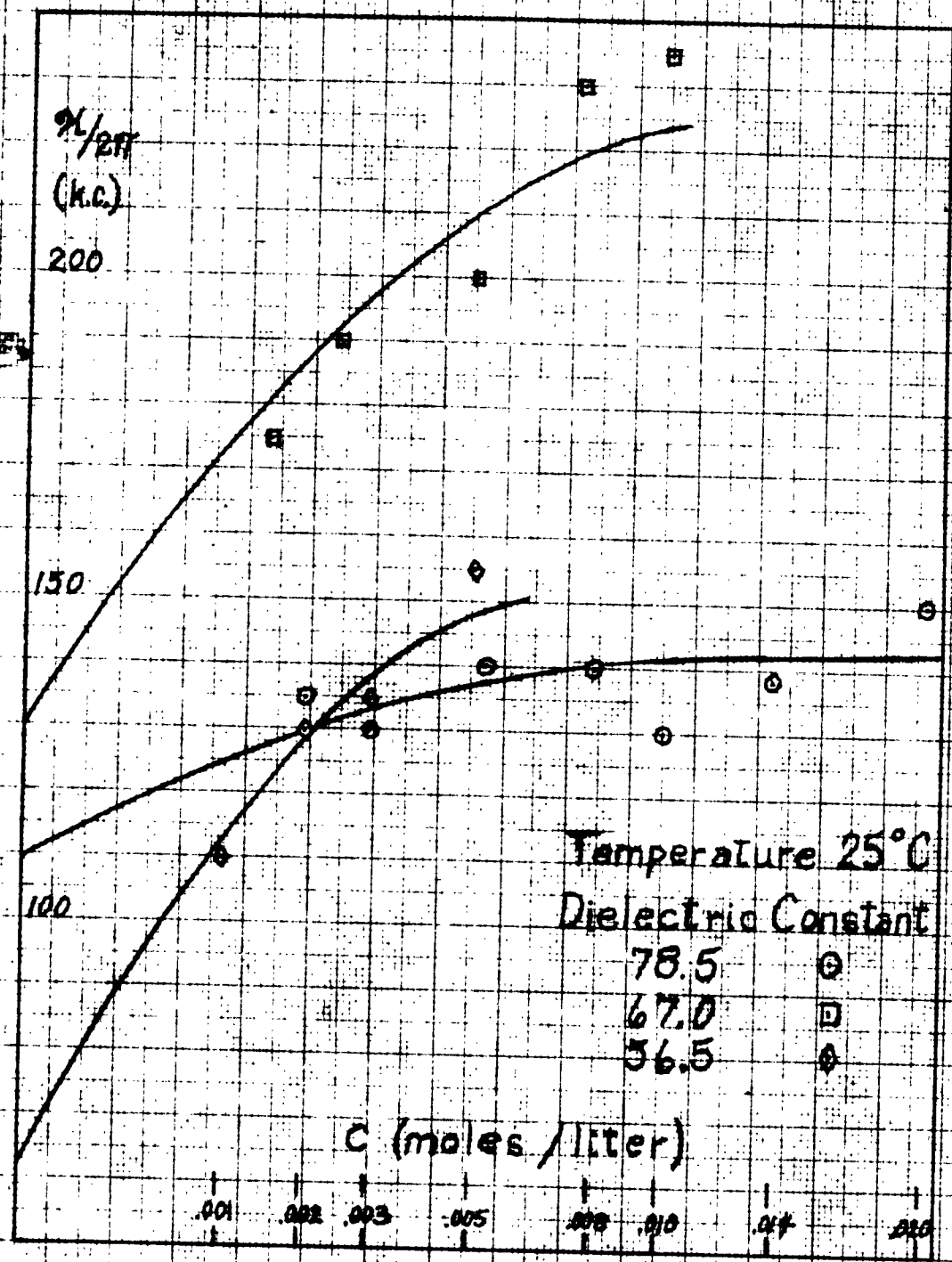
Dielectric constant 67.0 esu. $k_1/2\pi = 130$ kc.

.0015	.00278	9.58
.002	.00228	11.2
.005	.00275	9.93
.0075	.00207	9.54
.010	.00201	9.60
	Average	10.0

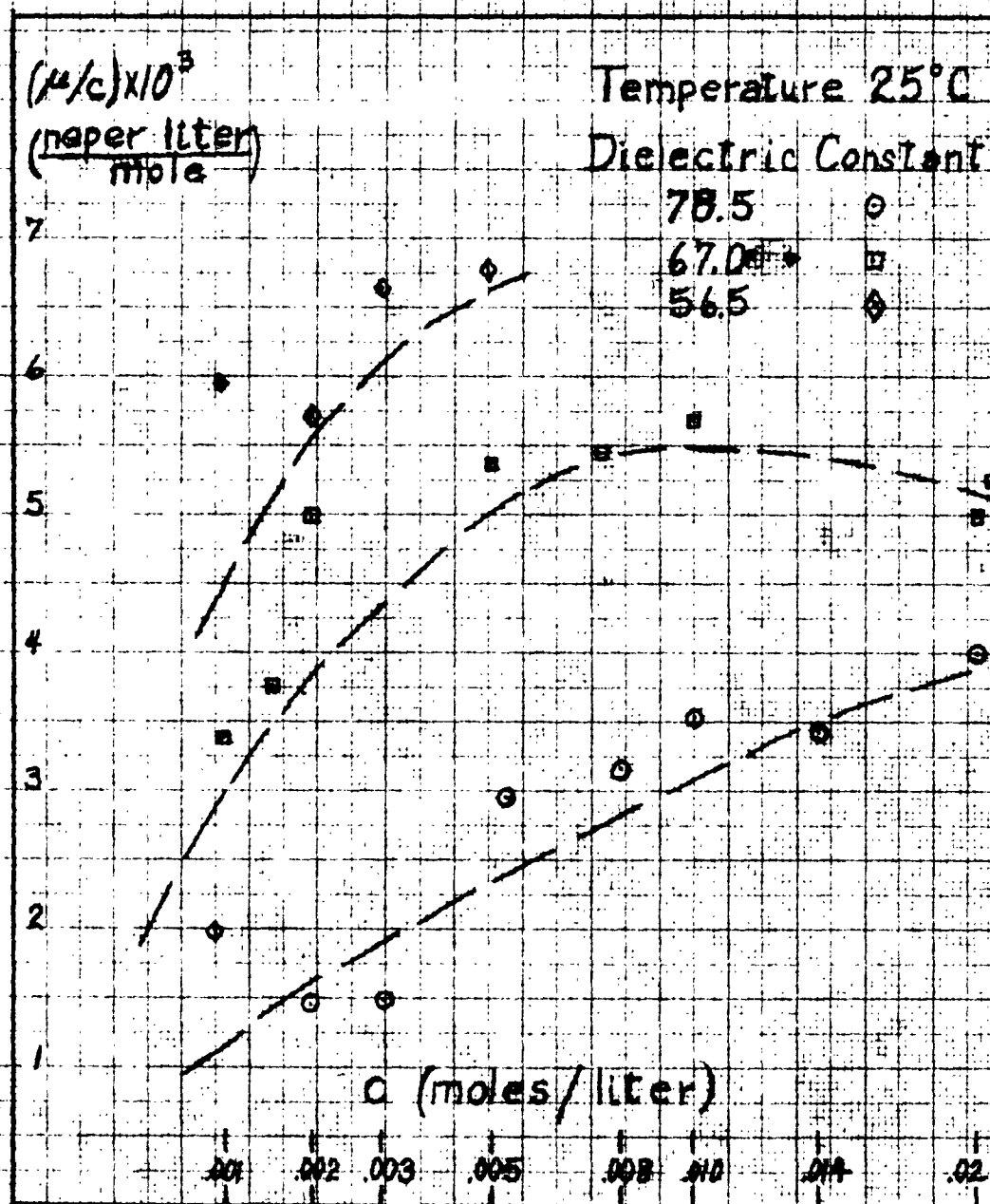
Dielectric constant 56.5 esu. $k_1/2\pi = 62$ kc.

.001	.000695	10.8
.002	.000627	9.56
.003	.000659	10.91
.005	.000590	10.7
	Average	10.0

Relaxation Frequency versus Concentration



Excess Absorption per Wavelength per Mole/Liter versus Concentration



Summary of Results

In order to be able to check the acoustic results for the values of dielectric constant used it was necessary to determine the values of the mass action equilibrium constant by another means. This was done by making conductivity measurements on dilute solutions of magnesium sulphate following the method described in Harned and Owen's *The Physical Chemistry of Electrolytic Solutions* [3].

Values for the mass action equilibrium constant for dioxane water mixtures having values of the dielectric constant equal to 67.0 esu (13.0% by weight dioxane) and 56.5 esu (25.0% by weight dioxane) were determined. This was done with conductivity measuring equipment which belonged to the Agriculture department. Dr. Appleman very kindly let the author use it.

The results of these measurements give for $D = 67.0$ esu $K = .00253$ and for $D = 56.5$ esu $K = .000694$. These measurements were made at approximately 25°C. See the appendix for details.

The results of the calculations for all solvents tested may be summarized as follows.

D (esu)	K (acoustic) (mole/liter)	K (conduct.) (mole/liter)	$k_1 \times 10^{-6}$ (sec. ⁻¹)	$k_2 \times 10^{-7}$ (sec. ⁻¹ liter mole ⁻¹)
78.5		.0063*	.69	11
67.0	.0024	.0025	.82	34
56.5	.00065	.00069	.39	60

* Taken from reference 6.

According to Laidler [17] the rate of change of the specific rate of reaction of a pair of reacting ions of valence z_1 and z_2 with the

reciprocal of the dielectric constant is given by the following equation:

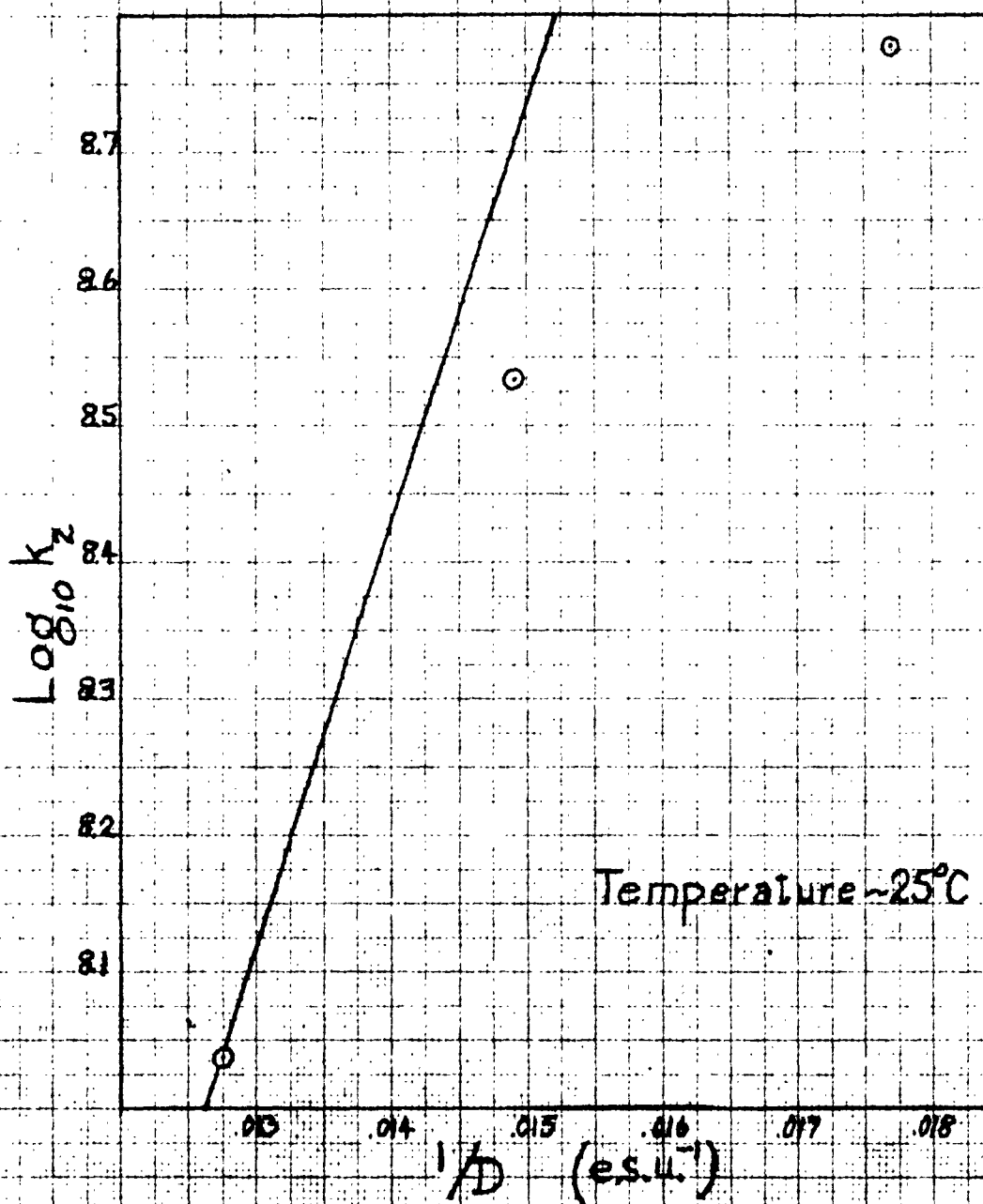
$$-\frac{d \ln k_2}{d (1/D)} = \frac{e^2 z_1 z_2}{kTr} \quad (30)$$

In our case $z_1 = -z_2 = 2$ and r equals twice the mean ionic radius 3.08×10^{-8} cm. The value of the slope is calculated as plus 312. The logarithm of the specific rate constant k_2 is plotted against the reciprocal of the dielectric constant and the theoretical slope is drawn in for comparison. The plot is on the next page.

It is seen from the plot that the specific rate of association does increase with the reciprocal of the dielectric constant as it should if ions of the opposite sign are involved as supposed here but apparently not in a linear fashion. The positive increase of k_2 gives further credence to the dissociation hypothesis.

e is the electrostatic unit of charge and k is Boltzmann's constant.

Specific Rate of Ion Association as a Function of Dielectric Constant



INFLUENCE OF THE IONAL CONCENTRATION

The investigation by Tamm of the effect on the excess sound absorption of magnesium sulphate solutions of adding sodium chloride furnishes a test of the influence of the ional concentration.

Calculations based upon approximate equations derived by K. Laidler [17] for the dependence of reaction rate upon ionic strength (equal to $2f^2$) were used to calculate α as a function of the ratio of concentration of sodium chloride to concentration of magnesium sulphate. The equations apply strictly only at very low concentrations so that agreement with experiment is only qualitative. Calculated values of $\Delta\mu/\mu$ for a concentration of magnesium sulphate of 0.1 molar are compared with the values expected according to Tamm's rule in the Table below.

SALT EFFECT		
$\frac{C_{NaCl}}{C_{MgSO_4}}$	$\frac{\Delta\mu}{\mu}^a$	$\frac{\Delta\mu}{\mu}^b$
0	0	0
1.57	.170	.314
3.93	.617	.785
6.26	1.62	1.25
8.73	2.10	1.75
11.2	2.41	2.24

a. Calculated using equation (24) and approximate values of α .

b. Calculated using Tamm's rule.

INFLUENCE OF THE TEMPERATURE

It is well known that the specific rate constants are exponentially dependent upon the temperature [17]. Referring to equation (25) one sees that the temperature dependence of κ should thus be determined by the temperature dependence of the specific rate of molecular dissociation. The linear dependence of the $\log \kappa$ on the reciprocal of the absolute temperature reported by Tamm [2] and by Wilson [4] is thus explained. The experimental activation energy estimated by Tamm and by Wilson is apparently the activation energy of molecular dissociation.

The term multiplying k_1 in equation (25) should vary only slightly with temperature since according to the Debye-Huckel theory the temperature always appears multiplied by the dielectric constant. In the range of temperatures from 0°C to 80°C the product DT varies by only 10%. Thus both α and $F\alpha$ should change very little. Any slight change with temperature should be masked by the exponential behavior of k_1 . In particular k_1/κ should be approximately constant in this temperature range.

Tamm reports a detailed series of measurements for a .05 molar solution of MgSO_4 from 11°C to 80°C. The value of α for a .05 molar may be calculated as mentioned above in the discussion of the water solvent results. The values of the compressibility over this range of temperatures may be estimated from the speed of sound as a function of temperature. The expected values of μ for this concentration and this range of temperatures have been calculated using the average value of $W = 9 \times 10^{-3}$ for water and are given in the table below. The calculated values are to be compared with values estimated from Tamm's published results.

TEMPERATURE EFFECT

Temp. °C	$\mu \times 10^4$ (calculated)	$\mu \times 10^4$ (estimated from Tamm's work)
0	1.85	-
10	1.90	1.8
20	1.94	1.9
30	1.94	2.0
40	1.93	1.9
50	1.90	1.8
60	1.86	1.5
70	1.82	-
80	1.76	1.2

V. Conclusion

The calculated values of the rate constants k_1 and k_2 are thought to be accurate to two significant figures as given in the summary on page 31. This judgment is based upon the self consistency of the calculated values of the ratio K for the different concentrations used in the acoustic method and upon the good agreement between the two different methods of determining K .

Calculations were also carried out using a somewhat larger value for the mean ionic diameter of 3.64 angstroms taken from the work of Harned and Hudson on the diffusion of aqueous magnesium sulphate solutions [12]. It was found that the results for the aqueous magnesium sulphate solutions were unchanged while the calculated values of K for the dioxane water mixtures were slightly increased to give a little better agreement with the values of K determined from conductivity measurements. The increase in individual values of K calculated for each concentration was, however, less than the variation between individual values. From this we may conclude that k_1 and k_2 are insensitive to the exact value of the mean ionic diameter to the degree of accuracy attained here.

The fact that the relaxation frequencies for MgSO_4 , MgS_2O_3 and MgCrO_4 are all about the same and different for NiSO_4 , ZnSO_4 and

MgSO_4 in water solutions as determined by Tamm seems to indicate that k_1 the rate of molecular dissociation is largely determined by the positive metal ion rather than by the negative ion. Further, it appears from the unusual behavior of k_1 with the addition of dioxane that the nature of the solvent has quite an important effect upon the rate of dissociation. Perhaps a continued study along the lines suggested in this thesis might shed more light upon the factors determining rate processes involving molecular dissociation.

VI. Bibliography

1. G. Kurtze, Nachrichten, Der Akademie Der Wissenschaften In
Gottingen, Mathematische- Physikalische Klasse (1952) No. 9
2. K. Tamm, same No. 10
3. The Physical Chemistry of Electrolytic Solutions, second edition
(1950) by H. Harned and B. Owen (Reinhold Publishing Corp.)
4. O. B. Wilson Jr., Technical Report No. IV, Dept. of Physics
U. C. L. A. (1951)
5. R. W. Leonard, Technical Report No. I, Dept. of Physics
U. C. L. A. (1950)
6. R. W. Money and C. W. Davies, Trans. Faraday Soc., 28, 609 (1932)
7. Leonard Liebermann, Physical Review 76, 152 (Nov. 15, 1949)
8. Romard Barthel, J. A. S. A. 24, 313 (1952)
9. Leonard Liebermann, Physical Review 75, 1415 (May 1, 1949)
10. R. E. Barrett and R. T. Beyer, Physical Review 84, 1060 (1951)
11. W. H. Banks, Chemical Society (London), 3341 (1931)
12. H. S. Harned and R. M. Hudson, J. Am. Chem. Soc. 73, 5880 (1951)
13. Charles J. Burton, J. A. S. A. 20, 186 (1948)
14. C. J. Moen, J. A. S. A. 23, 62 (Jan. 1951)
15. G. Kurtze and K. Tamm, Acustica 3, 33 (1953)
16. C. E. Mulders, Appl. Sci. Res. B1., No. 5, 341 (1950)
17. Chemical Kinetics (1950) by k. Laidler (McGraw Hill)
18. J. B. Hasted, Ritson and Collie, J. Chem. Physics 16, 1 (1948)
19. Statistical Thermodynamics (1939) by R. Fowler and E.
Guggenheim (MacMillan Co.)

APPENDICES

Derivation of Equations (24) and (25)

Consider a solution containing ions A and X of one sign, ions Y and B of opposite sign and the neutral molecules AB. Let it be supposed that the ions A and B are continually associating to form AB and that the molecules AB are continually dissociating into the ions A and B. The ions X and Y remain unassociated and merely insure electrical neutrality of the solution. Introducing the specific rate constants and the mean activity coefficient squared, the expression for the rate of production of ions A (or of B) may be written as

$$d(A)/dt = k_1(AB) - k_2 f_{\pm}^2(A)(B) \quad (1)$$

When equilibrium is attained, $d(A)/dt = 0$.

If it is supposed that the equilibrium between AB and A and B is pressure dependent, then a change in the pressure will cause a shift in the equilibrium. Such a medium may be characterized as having a complex compressibility. The isothermal compressibility of the solution may be assumed to be equal to the isothermal compressibility of the solvent (assumed real) plus a complex factor due to the perturbed chemical equilibrium. Thus

$$\beta = \beta_0 + \beta' \quad (2)$$

It may be shown as follows that the contribution to the intensity attenuation coefficient per wave length of the complex compressibility is

$$2a\lambda = -2\pi \operatorname{Im} (\beta'/\beta_0)$$

Define the complex sound velocity v by the equation

$$\frac{1}{v} = \frac{1}{v_0} + \frac{a}{i\omega}$$

The term v_0 is the zero frequency sound velocity since a goes to zero as ω^2 . This corresponds to a plane wave with time dependence of the form $\exp(i\omega t)$.

Transpose the v_0 and square the expression.

$$\frac{v_0^2}{v^2} = 1 - \frac{a^2 v_0^2}{\omega^2} - \frac{12av_0}{\omega}$$

On the other hand,

$$\frac{v_0^2}{v^2} = \frac{\beta}{\beta_0} = \frac{\beta_0 + \beta'}{\beta_0}$$

Therefore

$$\operatorname{Im} \left(\frac{\beta_0 + \beta'}{\beta_0} \right) = \operatorname{Im} \frac{\beta'}{\beta_0} = - \frac{2av_0}{\omega} = - \frac{2a\lambda}{2\pi}$$

The quantity $2a\lambda$ has a maximum value when taken as a function of the frequency which occurs at the so called relaxation frequency. If the maximum excess sound absorption per wave length is represented by μ , then

$$\mu = -2\pi \max \operatorname{Im} (\beta'/\beta_0) \quad (3)$$

Consider a small unit cube in a homogeneous volume of solution. Let it be supposed that no molecules of solvent nor of solute get in or out of the cub, that the cube is in a plane sound field, and that the dimensions of the cube are small compared

to a wave length. The walls of the cube will pulsate uniformly with the passage of a sound wave. The rate equation (1) may be written in terms of the numbers of molecules and ions per unit volume as

$$dn_1/dt = k_1 n - k_2 f_+^2 n_1 n_2 \quad (4)$$

At equilibrium $dn/dt = -dn_1/dt = -dn_2/dt = 0$.

In writing the rate equation k_1 and k_2 are assumed to be independent of concentration while f_+^2 is assumed to be a function of the concentration. In a harmonic sound field all of the parameters n , n_1 , n_2 , k_1 , k_2 , and f_+^2 are assumed to be pressure dependent and to have a harmonic time dependence of the form $\exp(i\omega t)$.

The concentration of molecules and ions will vary with the passage of a sound wave because the numbers of ions and molecules vary and because the volume varies. Thus the variation in the unit volume must also be considered. The available data, however, seem to indicate that the volume variation makes a negligible contribution to the sound absorption.

The general irreversible rate equation may be represented by a Taylor's series in terms of small variations in all of the parameters. Only linear terms need be considered.

$$\begin{aligned} i\omega \Delta n_1 = & n \Delta k_1 - f_+^2 n_1 n_2 \Delta k_2 + k_1 \Delta n - k_2 f_+^2 (n_1 \Delta n_2 + n_2 \Delta n_1) + \\ & - k_2 n_1 n_2 \Delta f_+^2 - (k_1 n - 2k_2 n_1 n_2 f_+^2) \Delta v \end{aligned} \quad (5)$$

Since it takes one ion each of A and B to make one molecule of AB, it is true that

$$\Delta n = -\Delta n_1 = -\Delta n_2 \quad (6)$$

The mass action equilibrium law,

$$K = k_1/k_2 = f_{+}^2 n_1 n_2 / n_1 \quad (7)$$

gives

$$n \Delta k_1 - f_{+}^2 n_1 n_2 \Delta k_2 = k_2 f_{+}^2 n_1 n_2 \Delta K / K \quad (8)$$

Well known thermodynamic relations [3] give

$$(\partial \Delta \phi / \partial p)_T = \Delta V,$$

and $\Delta \phi_0 = -RT \ln K$

Thus, $RTK^{-1} (\partial K / \partial n) (\partial n / \partial p)_T = -\Delta V_0,$

and therefore

$$\Delta K / K = (\Delta V_0) \Delta n / RT (\partial n / \partial p) \quad (9)$$

Since $\Delta \phi_0$ is the free energy change when all of the reactants are in their standard state and is not the free energy change on going from the ionized state to the molecular state, the associated molal volume change ΔV_0 will be treated as an empirical constant. This is contrary to the assumption made by L. Liebermann [7] in an earlier paper.

The contribution β' to the isothermal compressibility due to a perturbation of the dissociation process is

$$\beta' = - (\partial v / \partial n) (\partial n / \partial p)_T$$

Define $\Delta V = N (\partial v / \partial n)_T$, then

$$(\partial n / \partial p)^{-1} = - (\Delta V) / N \beta' \quad (10)$$

Unit volume has been assumed so that v is suppressed.

Putting equations (9) and (10) into equation (8) gives

$$n \Delta k_1 - f_{+1}^2 n_1 n_2 \Delta k_2 = k_2 f_{+1}^2 n_1 n_2 W \Delta n / \beta' NRT \quad (11)$$

where $W = (\Delta V_0)(\Delta V)$.

To estimate the variation in the unit volume with the passage of a sound wave consider the variations in volume, pressure, and number of molecules n , represented vectorially on the clock diagram below (Figure 1).

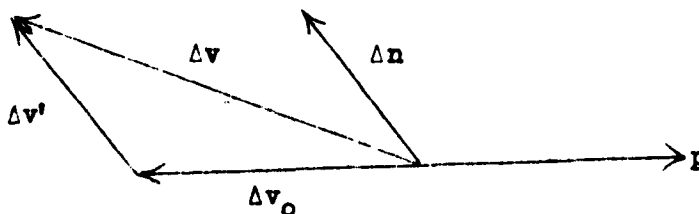


Figure 1

The net change in volume Δv must lag behind the acoustic pressure p since this gives work done on the system as positive.

Δv_0 is the variation in volume of the solvent assumed dissipationless for convenience so that it lags behind the acoustic pressure by one hundred and eighty degrees.

The variation in volume $\Delta v'$ due to a shift in equilibrium is assumed to be in phase with the variation in the number of molecules Δn . The resultant change in volume of the solution is Δv . A decrease in volume associated with the dissociation process has been assumed.

From the diagram it may be deduced that

$$\Delta v = -(\beta_0 + \beta') \gamma p ,$$

$$\Delta v' = -\beta' \gamma p .$$

The ratio of specific heats γ has been introduced because the process is adiabatic.

It may reasonably be assumed, however, that

$$\Delta v' = (\partial v / \partial n_2) \Delta n_2 = (\Delta V) \Delta n / N ,$$

since γ is very close to one.

Eliminating $\Delta v'$ and γp between the last three equations gives

$$\Delta v = (\Delta V) (\beta_0 + \beta') \Delta n / N \beta' \quad (12)$$

To estimate the variations in f_{\pm}^2 as a function of $\frac{\Delta n}{N}$ let a new function F be defined such that

$$F = - (Z_1^2 + Z_2^2) d (\ln f_{\pm}^2) / d \Gamma \quad (13)$$

This function is discussed in the following section.

Γ is called the ional concentration [3] and for the case considered here is given by the equation

$$\Gamma = N^{-1} \sum_{i=1}^4 n_i Z_i^2 \quad (14)$$

Variations in f_{\pm}^2 will be given by

$$\Delta f_{\pm}^2 = - f_{\pm}^2 F (\Delta n/N - \Gamma' \Delta V) \quad (15)$$

where $\Gamma' = \Gamma / (Z_1^2 + Z_2^2)$. Equation (6) and the fact that the populations of X and Y remain unchanged has been used.

Substitute equations (6), (11), (12), and (15) into equation (5). Cancel out Δn and solve for β' . Use equation (7) to eliminate terms involving k_2 .

$$\beta' = k_1 n N^{-1} [W(RT)^{-1} - (\Delta V) \beta_0 (F \Gamma' - 1)] [1\omega - \kappa]^{-1}.$$

$$\text{where } \kappa = k_1 [1 + n_1^{-1} + n_2^{-1} + n N^{-1} (F + \Delta V - F \Gamma' \Delta V)].$$

If one assumes that (ΔV) is very small so that $(\Delta V) \ll F$ and also $(\Delta V) \ll (\Delta V_0)$ then all terms involving (ΔV) may be dropped. The results seem to confirm these assumptions as will be shown below. Thus

$$\beta' = [k_1 n W / NRT] [1\omega - \kappa]^{-1}$$

$$\text{where } \kappa = k_1 [1 + n(n_1^{-1} + n_2^{-1} - N^{-1} F)]. \quad (16)$$

In reference [7] it was assumed that $(\Delta V) = (\Delta V_0)$.

β' has a maximum at $\omega = \kappa$ thus κ is the relaxation frequency.

To obtain expressions for μ and κ in terms of concentration units consider the following. Let c be the total concentration of A in either the molecular or ionized state and let α be the fraction of A in the ionized state, then

$$(AB) = c(1-\alpha) = nN^{-1},$$

$$(A) = c\alpha = n_1N^{-1}.$$

Similarly let c' be the total concentration of B in either state and let α' be the fraction of B in the ionized state, then

$$(AB) = c'(1-\alpha'),$$

$$(B) = c'\alpha'.$$

Thus
$$c(1-\alpha) = c'(1-\alpha').$$

Suppose that $c' = mc$ then solve for α'

$$\alpha' = 1 - m^{-1} + m^{-1}\alpha.$$

Thus
$$(B) = c(m-1 + \alpha) = n_2N^{-1}.$$

Substitute equation (16) into equation (3) and change the notation as indicated above. The expression for the maximum excess sound absorption per wave length in this notation is then given by

$$\mu = \pi c(1-a)k_1W/\kappa\beta_0RT. \quad (17)$$

Similarly in this notation the expression for the relaxation frequency κ becomes

$$\kappa = k_1\left[1 + \frac{1-a}{a} \left(\frac{2a+m-1}{a+m-1} - Fca\right)\right]. \quad (18)$$

For the special case where the concentration of magnesium ions equals the concentration of sulphate ions $m = 1$ and equation (18) becomes equation (25) of the text.

The Function Fca

The function F always appears multiplied by ca so that it is more convenient to consider Fca rather than F alone.

The expression for the mean activity coefficient squared according to the Debye-Huckel theory is

$$\ln f_{\pm}^2 = -4.606 S r^{1/2} (1 + \mu r^{1/2})^{-1}. \quad (19)$$

For a bi bivalent electrolyte where $z_1 = z_2 = 2$ and taking for the mean ionic diameter the standard value of 3.08 angstroms [19], the expressions for S and μ are

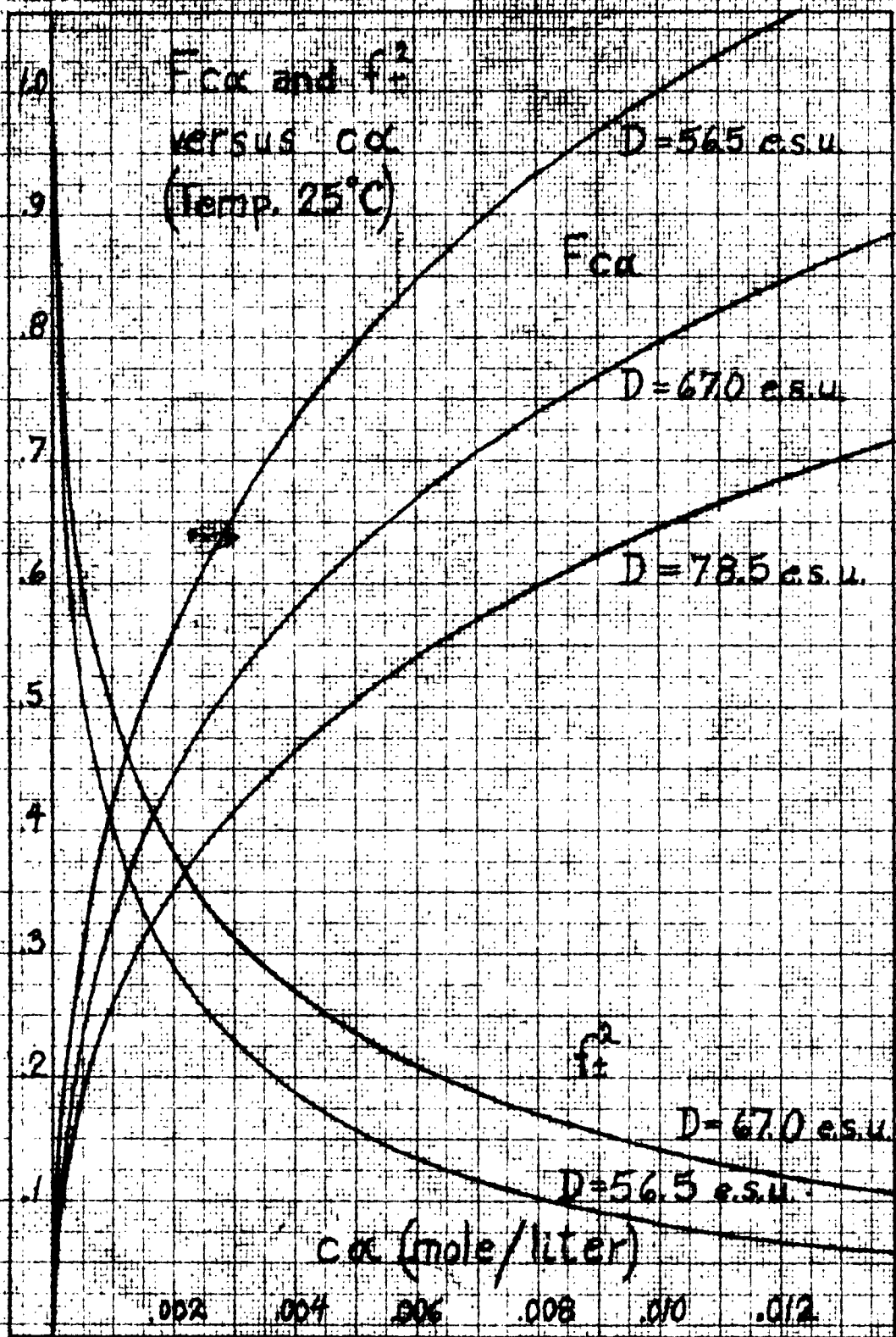
$$S = 5.132 \times 10^6 (DT)^{-3/2},$$

$$\mu = 109.6 (DT)^{-1/2}.$$

Substitute equation (19) into equation (12) and multiply through by ca .

$$Fca = 18.424 S ca r^{-1/2} (1 + \mu r^{1/2})^{-2} \quad (20)$$

Equations (19) and (20) are plotted on page 52 for several values of the dielectric constant as a function of ca over the range of values of c in which these equations are expected to hold approximately.



Preparation of the Samples

In preparing the samples the resonator was first washed with cleaning solution (concentrated sulphuric acid and potassium chromate) and then washed with a detergent and hot water. The resonator was finally rinsed several times with once distilled water.

In preparing the solvent mixture, once distilled water and dioxane (Baker Chemical Co., Technical grade) were weighed and mixed in the resonator. The weights were determined to four significant figures on a large kilogram scale so that the percentage by weight of dioxane was known accurately. The dielectric of the solution was determined from this knowledge by means of a table [3].

It has been found that any gas bubbles on the walls of the resonator will enormously increase the decay time and may in fact mask all other sources of attenuation. It was necessary to prevent the formation of any such bubbles. For this purpose the sample was run through a degassing process.

The sample was connected by means of a short length of rubber tubing which had been previously boiled in concentrated sodium hydroxide solution and a glass tube adapter to an evacuated 12 liter sphere. A magnetostrictive transducer was held tightly against the resonator and driven at about its resonant frequency and the fifth resonant spherical mode of the resonator. This was about 26 kc. Under these conditions a small amount of liquid (about 1 gram) boiled off until the partial pressures of liquid and liquid vapor were equal. The gas in solution continued to come out of solution, expe-

dited by the action of the strong acoustic field built up at the resonant mode of the bottle until the partial pressure of the gas in the gas phase was equal to the partial pressure of the gas dissolved. When the gassing of the solution slowed down appreciably the second sphere was pumped out again. In this way the gas content of the solution was reduced to a small value so as to prevent the formation of any gas bubbles on the walls of the resonator during the series of reverberation measurements. The liquid was called degassed when no more bubbles could be driven out of the liquid, and sealed by means of a short rubber tube and a clamp. The process took about 36 hours on the average. The sample was then allowed to set for a couple of days so that any residual gas bubbles might redissolve.

To prevent the formation of gas bubbles due to the action of bacteria the samples were poisoned with a very small quantity of mercuric chloride. Four milliliters of a solution of 40 milligrams of mercuric chloride per liter were added to the 12.5 liters of solution in the resonator for this purpose.

The magnesium sulphate used was of the type Baker Analyzed and was weighed on an analytic balance to the last milligram thus giving four significant figures for the weight determination. To add the salt to the degassed liquid it was put in a one liter sphere which was coupled to the resonator. The sphere was then evacuated for several hours and a heat lamp was used to drive off gas sticking to the crystals. The two spheres were then opened to each other and the salt dissolved. Alternately the salt was merely added by opening the resonator and then degassing it again. The latter method was found

to be most efficient.

For convenience in weighing hydrated magnesium sulphate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was used for all of the low concentrations. It was estimated that the resulting change in the concentration of water in the solution was no greater than a few hundredths of one per cent. At higher concentrations anhydrous MgSO_4 was used. The values of the dielectric constant, estimated to three significant figures by means of the table mentioned above did not change on addition of the magnesium sulphate.

Conductivity Determinations of the Mass

Action Equilibrium Constants

The test cell was made of a pair of one centimeter square platinized parallel plates approximately one centimeter apart set in a small glass sphere. The test solution could be drawn up into the cell by means of a rubber bulb on the top. The bridge was a Conductivity Bridge Model RC 16 made by Industrial Instruments, Inc.

To make the test samples approximately two liters of solvent of the correct proportions of dioxane and water was prepared. From this approximately one liter of magnesium sulphate solution of maximum concentration was prepared. Finally from the solution and the pure solvent all of the other test samples were prepared in 250 ml. lots. One liter of a standard solution of .01 N KCl was also prepared.

The solution to be tested was drawn up into the test cell and the resistance was read on the bridge. The resistance of all of the

various solutions of magnesium sulphate as well as of the pure solvent and the standard solution were determined one after the other.

The resistance of the standard solution was used to calculate the cell constant. The specific resistance of the test solution was taken from the Handbook of Chemistry and Physics (1951). Once the cell constant had been determined in this fashion the specific conductivities of the various solutions were computed. To determine the specific conductivity of the magnesium sulphate in solution the specific conductivity of the magnesium sulphate L^* was taken as equal to the difference between the specific conductivity of the solution and of the solvent. The equivalent conductivity of magnesium sulphate in solution Λ is the specific conductivity of the magnesium sulphate times 1000 divided by the number of equivalents (twice the molar concentration) per liter. This quantity is plotted as a function of the square root of the concentration of salt.

To determine the mass action equilibrium constant from these measurements it is assumed that the Onsager conductance limiting law describes the behavior of an ideal completely dissociated salt. The difference between the theoretical and experimental conductance then is attributed to incomplete dissociation. (See reference 3 for a discussion of this assumption.)

When incomplete dissociation is taken into account the Onsager conductance law takes the form

$$\Lambda = \alpha \left[\Lambda_0 - (\alpha^* \Lambda_0 + \beta^*) \sqrt{\alpha} \right]$$

where for the 2-2 electrolyte

$$\Lambda = 1000L^*/2c$$

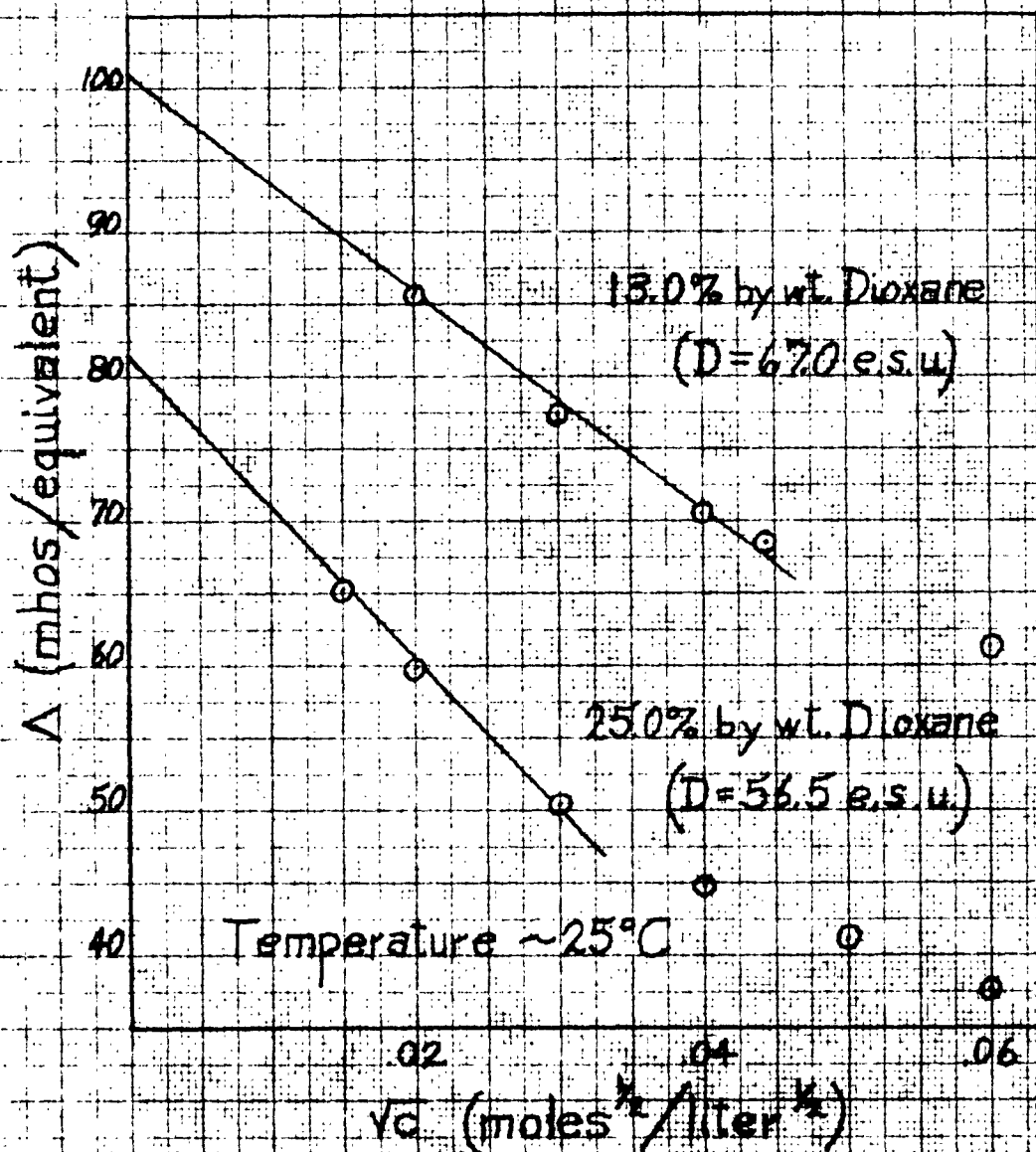
and Λ_0 is the value of Λ extrapolated to zero concentration. α^* and β^* are constants which are functions of the dielectric constant, the temperature and the viscosity of the medium (see reference 3, chapter 5).

In practice one plots Λ as a function of \sqrt{c} then extrapolates a straight line through the last few points to zero concentration to determine the limiting conductance Λ_0 . Then one computes α for each concentration tested and the corresponding activity coefficients. Then one computes the mass action equilibrium constant. One adjusts the extrapolated value of Λ_0 until one finds the value which gives the most nearly constant value of the mass action equilibrium constant. This was done and a plot of the experimental conductance with the limiting behavior indicated appears on the following page. The values of the various constants used and calculated are summarized in tables on page 59.

For the purpose of calculating K from the experimental values of the specific conductivity a method suggested by Banks [11] was employed. For the purpose of this study it was necessary to consider higher order terms which he neglects in his development.

The calculated values of K do not depend upon the choice of the mean ionic radius since the contribution of the term involving it is negligible in the range of concentrations used. Equation (21) was used in the form

Equivalent Conductivity versus Square Root of the Concentration for Dioxane Water Solutions of Magnesium Sulphate



$$\log r_{\pm}^2 = -2S' \sqrt{ca}$$

where the values of S' are given in the summary below.

Onsager Law Constants

% by wt. dioxane	Viscosity $\times 10^3$ (cgs)	D (esu)	α^*	β^*	S'
13.0	11.53 ^a	67.0	2.31	201.0	5.145
25.0	14.01	56.5	2.98	179.8	6.64

^a Viscosities were interpolated from a table on page 544 of ref. 3

Conductance Results (temperature 25°C)

$c \times 10^3$ (moles/liter)	Λ (mho/equiv.)	α	r_{\pm}^2	$K \times 10^2$ (moles/liter)	
13.0% by weight dioxane, D=67.0 esu					
0.00	102.	1.00	1.000	.253	average
0.40	85.8	.915	.636	.250	
0.90	77.5	.862	.517	.250	
1.593	70.6	.819	.425	.250	
1.963	68.7	.810	.390	.264	
3.60	61.5	.778	.286	.274 ^a	
25.0% by weight dioxane, D=56.5 esu					
0.00	83.	1.00	1.000	.0694	average
0.225	65.3	.920	.656	.0685	
0.40	60.0	.892	.580	.0714	
0.90	50.5	.695	.465	.0662	
1.60	44.8	.641	.376	.0687	
2.50	41.2	.611	.302	.0722	
3.60	37.7	.590	.244	.0744 ^a	

^a These values were ignored in computing the average since their large departure from the average was taken as an indication that the Onsager limiting equation did not apply well at these concentrations. (See reference 3)

Determination of the Isothermal Compressibility

The isothermal compressibility β appears in equation (23) and must be evaluated for the mixtures of dioxane and water considered. The following method was employed for this purpose.

The velocity of sound v_0 is related to the specific heats C_p and C_v , the density ρ and the isothermal compressibility β by

$$v_0^2 = \frac{C_p}{C_v \rho \beta} \quad (1)$$

On the other hand as was pointed out to the writer by Dr. Scott we have the thermodynamic relation

$$C_p - C_v = -T \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P^2 \quad (2)$$

This can be written in terms of the compressibility to give

$$C_p - C_v = \frac{T}{V\beta} \left(\frac{\partial V}{\partial T} \right)_P^2 \quad (3)$$

From rough calorimetric measurements on mixtures of dioxane and water the corresponding values of C_p were determined. From tables of the density of various mixtures of dioxane and water as a function of temperature given in Harned and Owen [3] the corresponding values of $(\partial V / \partial T)_P$ were estimated. Finally, from measurements of the velocity of sound in mixtures of dioxane and water [13] the corresponding values of v_0 were determined. By solving equations (1) and (3) simultaneously values for β and C_p / C_v were determined. The following table summarizes the results.

Compressibility Determination (25°C)

% weight dioxane	C_p/C_v	$\beta \times 10^{13} (\text{c.g.s.})$
0.0	1.00	455
12.0	1.03 ^a	437 ^b
20.0	1.05	420
32.6	1.08 ^a	425 ^b
45.0	1.11	438

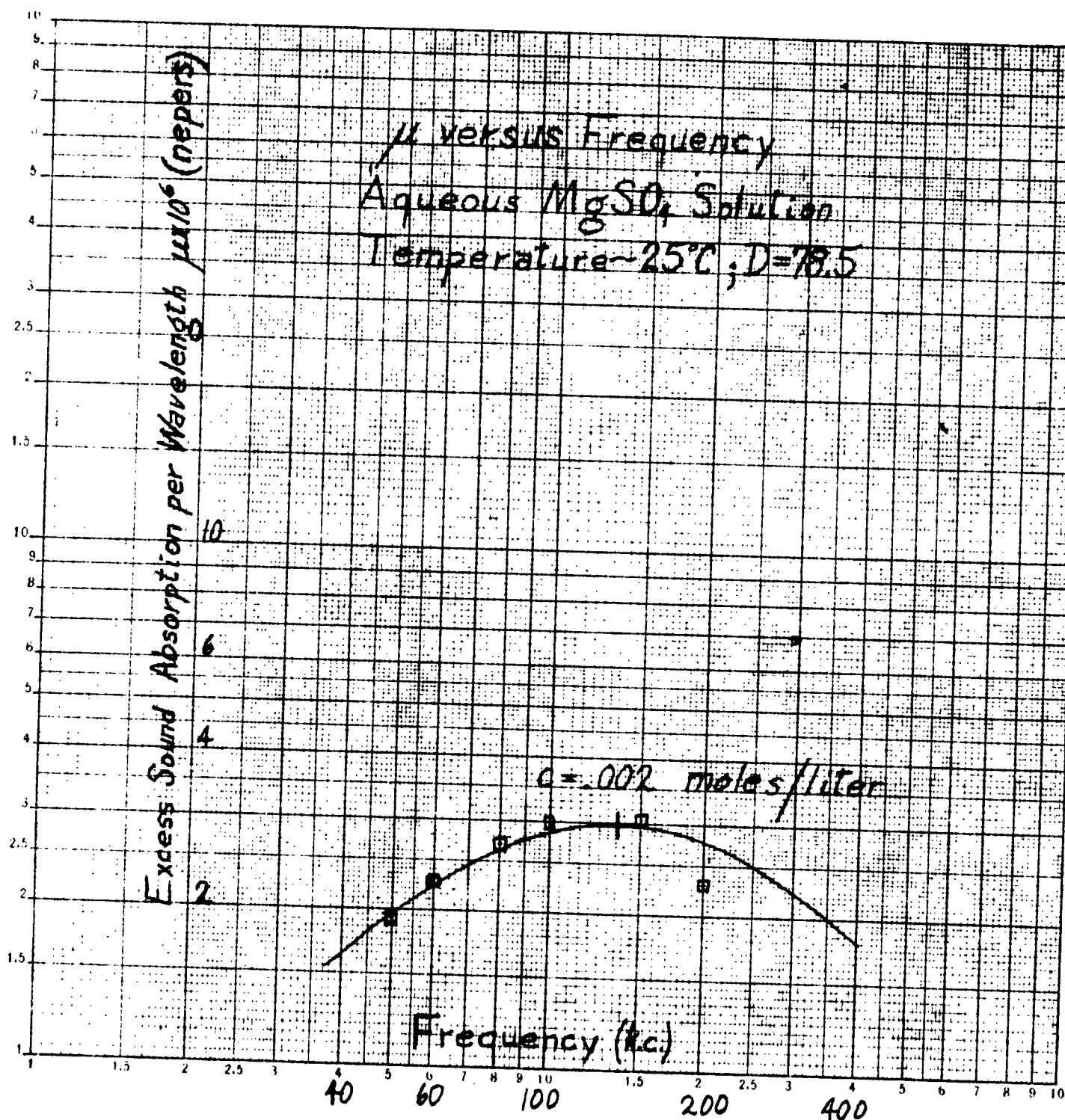
^a Interpolated values.

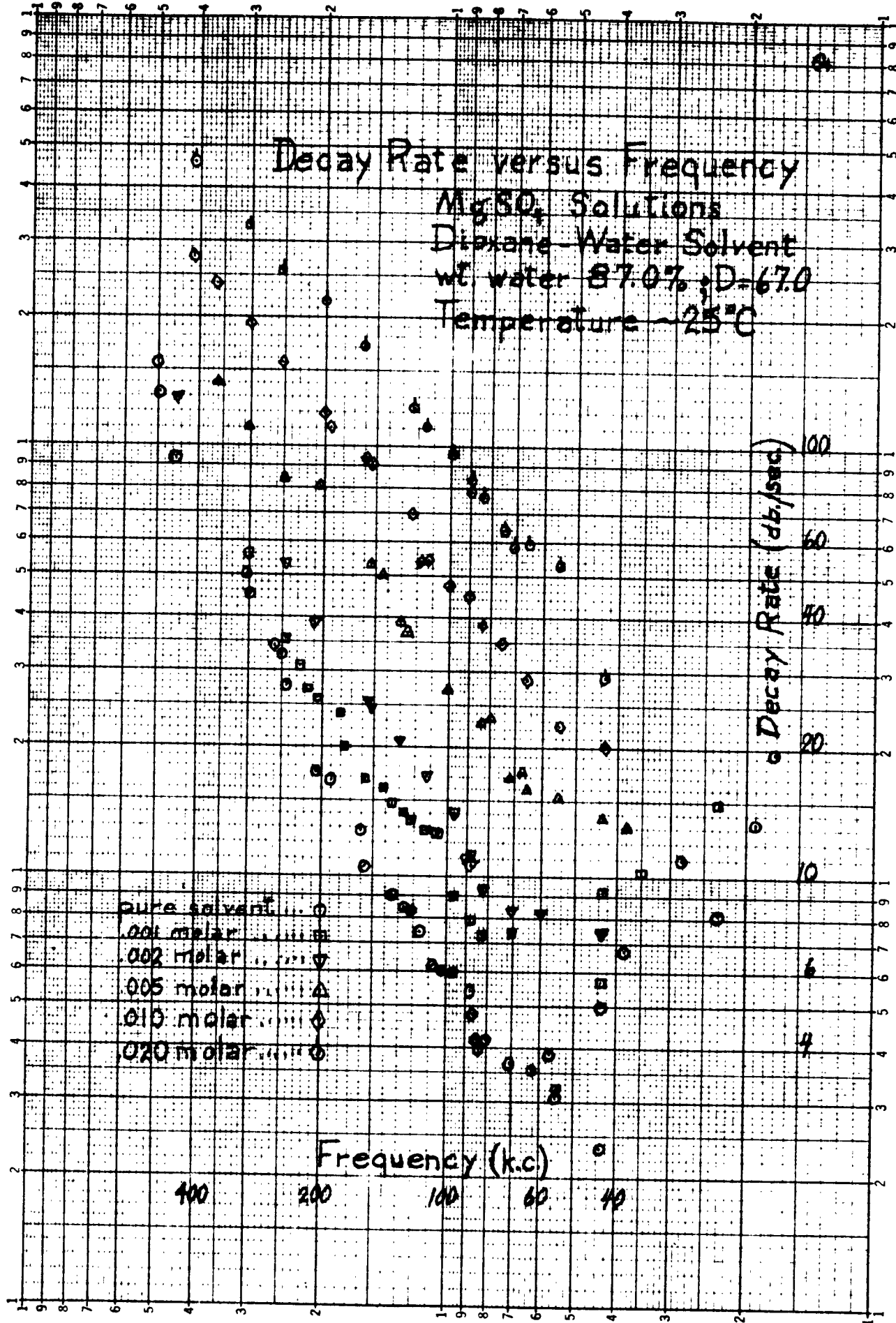
^b Calculated values using interpolated C_p/C_v .

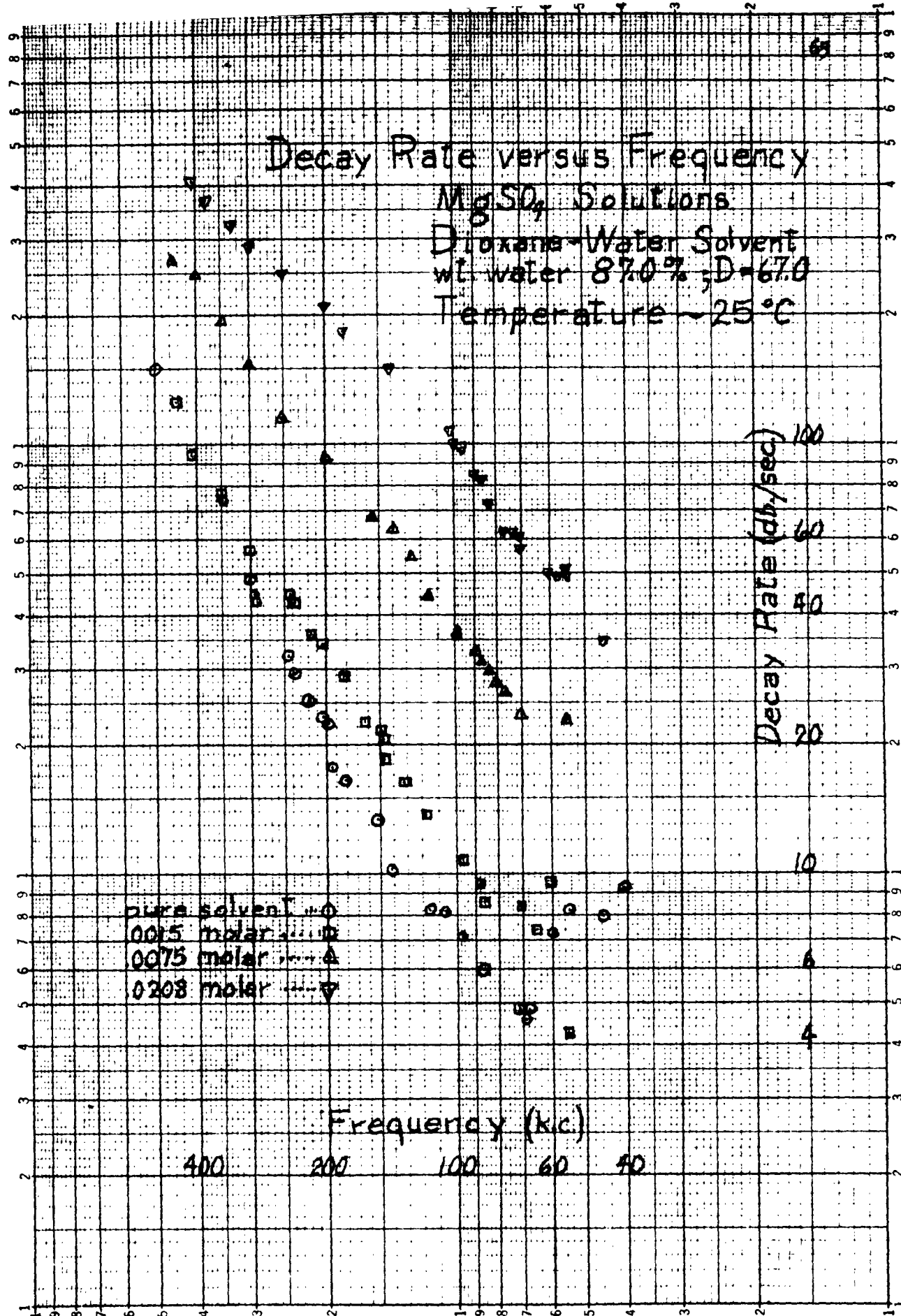
Summary of Acoustic Measurements
(Temperature 25°C)

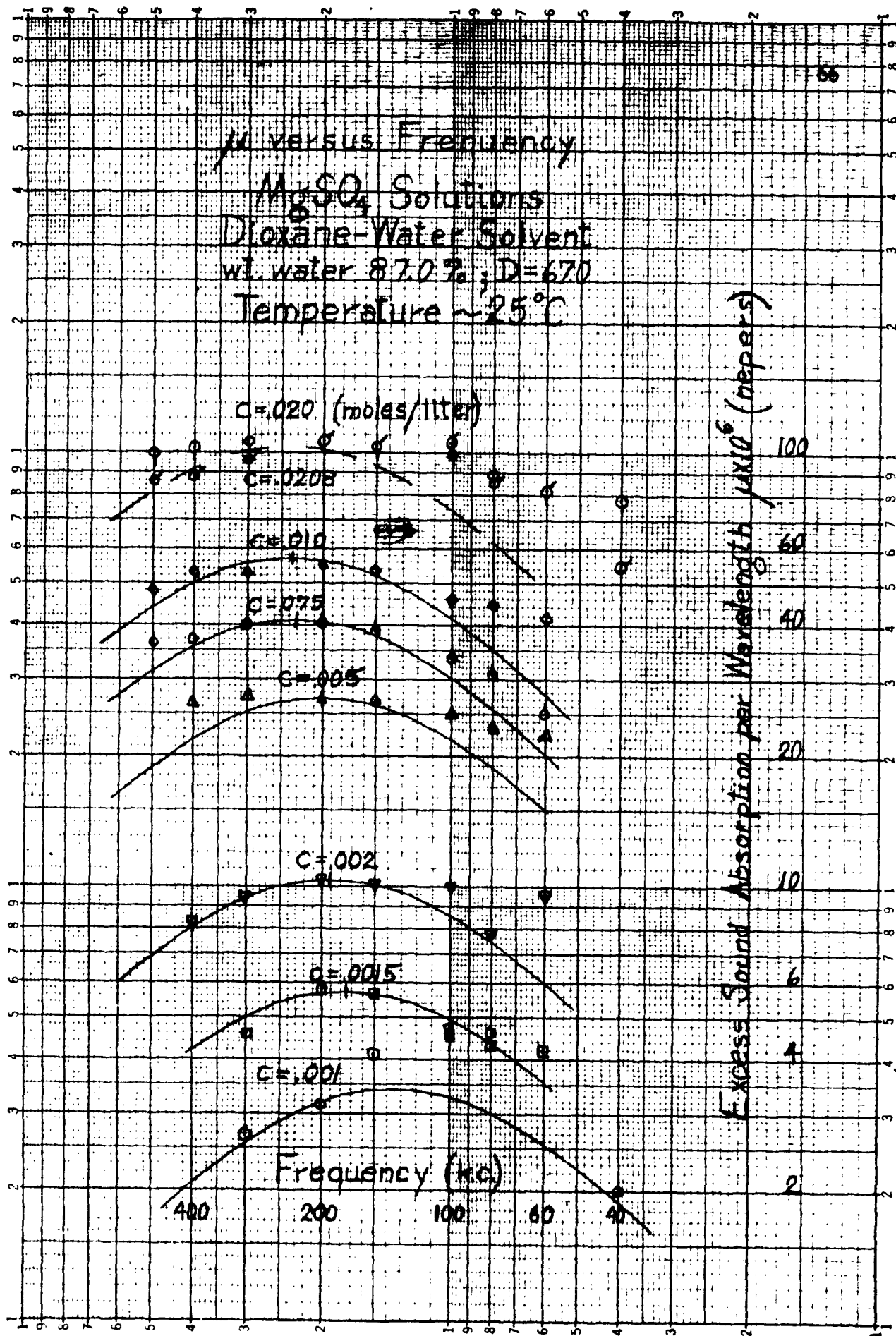
D (e.s.u.)	$\beta \times 10^{13}$ (c.g.s.)	c moles/liter	$\mu \times 10^6$	$\mu/c \times 10^3$ liter/mole	$\kappa/2\pi$ (K.c.)
78.5 (water)	455	.002	3.0	1.50	135
		.003*	4.5	1.53	130
		.0052*	15.5	2.98	140
Wilson's data [4]		.008	25.5	3.18	140
		.010*	35.5	3.55	130
		.014*	48.	3.43	138
		.020*	80.	4.00	150
67.0 (water-dioxane 13.0% by wt. diox.)	435	.001	3.4	3.4	
		.0015	5.7	3.82	175
		.002	10.0	5.02	190
		.005	27.	5.39	200
		.0075	41.	5.47	230
		.010	57.	5.70	235
		.020	100.	5.00	--
		.0208	110.	5.29	--
56.6	420	.0009	2.		--
		.001	6.0	6.00	110
(water-dioxane 25.0% by wt. diox.)		.002	11.5	5.75	130
		.003	20.0	6.67	135
		.005	34.0	6.80	155

μ versus Frequency
 Aqueous $MgSO_4$ Solution
 Temperature $\sim 25^\circ C$; $D = 78.5$







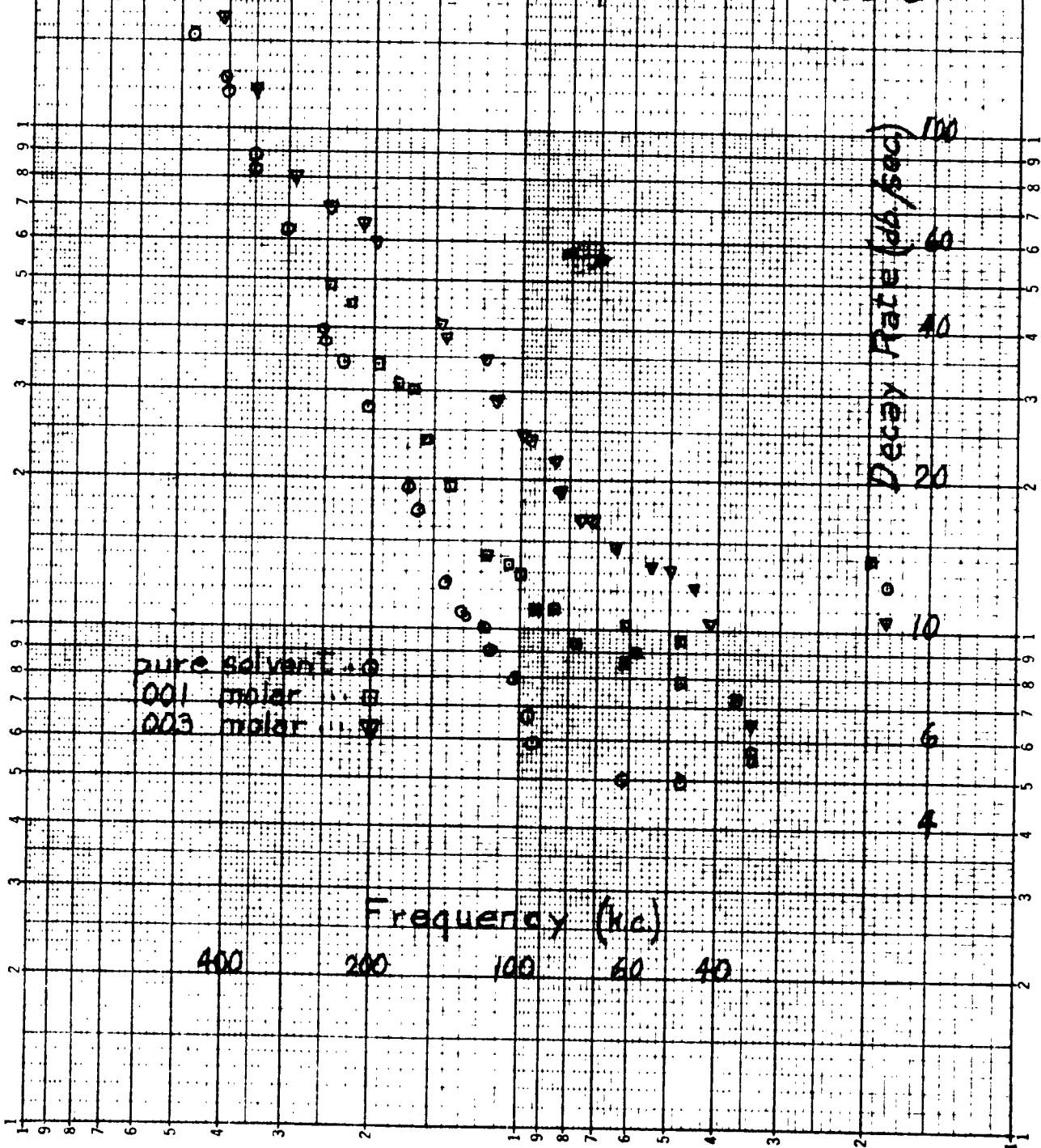


Decay Rate versus Frequency

MgSO₄ Solutions

Dioxane-Water Solvent
 wt. water 75.0%; D-565

Temperature ~ 25°C



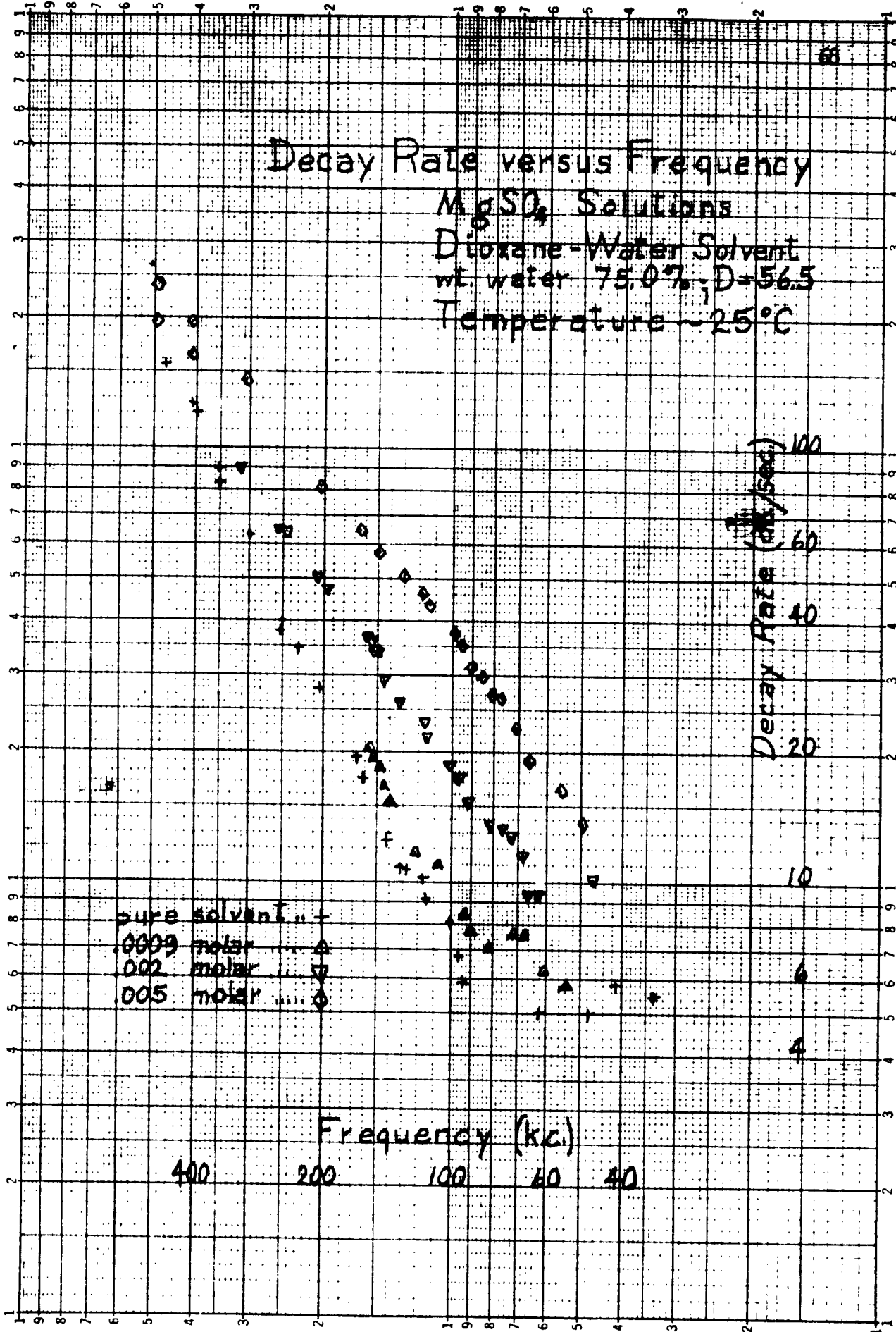
Decay Rate versus Frequency

MgSO₄ Solutions

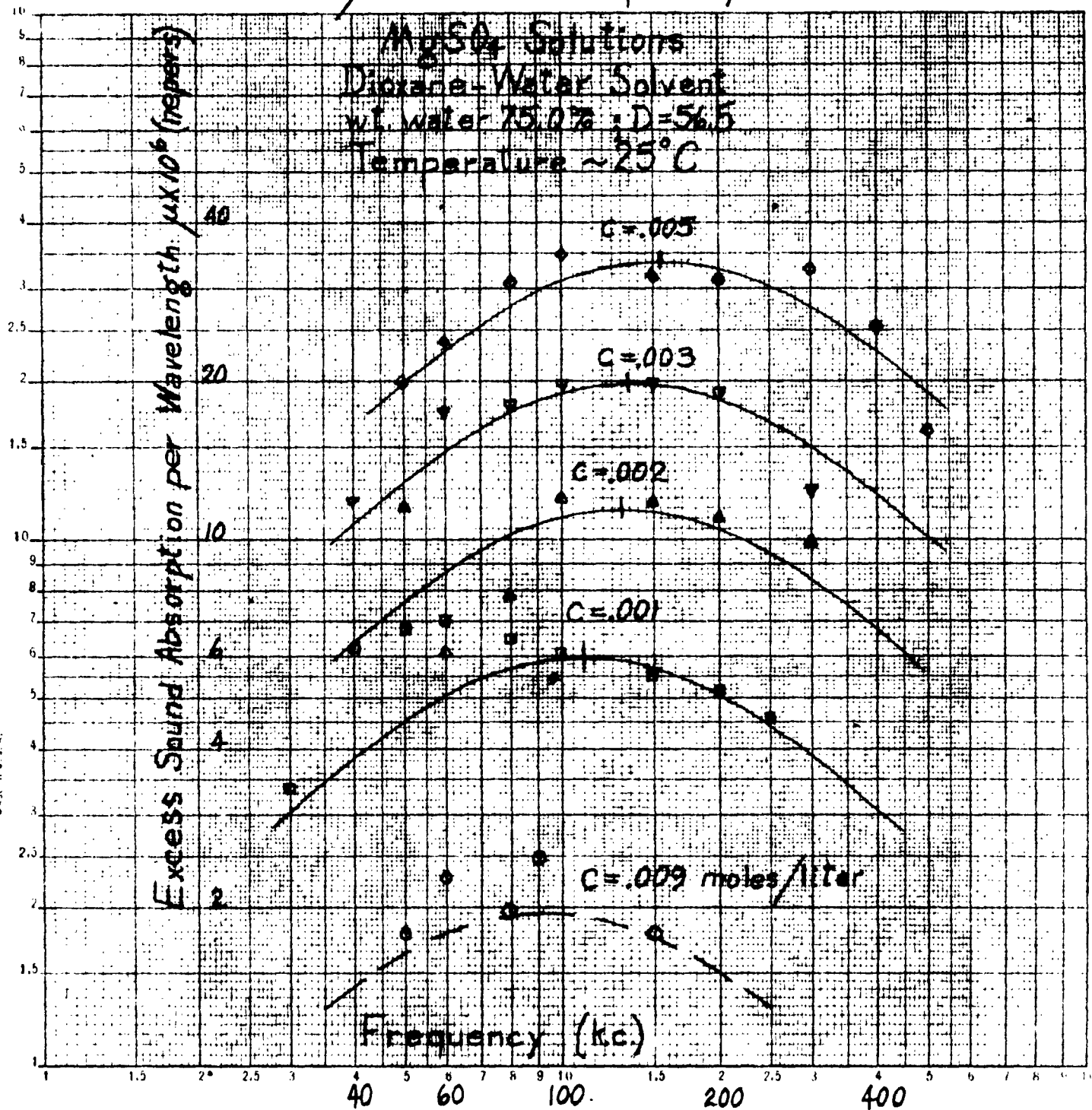
Dioxane-Water Solvent

wt. water 75.0%; D=56.5

Temperature ~25°C



μ versus Frequency



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